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Title: Uranium Corrosion From the perspective of surface science
investigations Early stage oxidation of uranium Early stage hydriding
corrosion of uranium

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Uranium Corrosion

From the perspective of surface science investigations

Early stage oxidation of uranium

Early stage hydriding corrosion of uranium

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W-9

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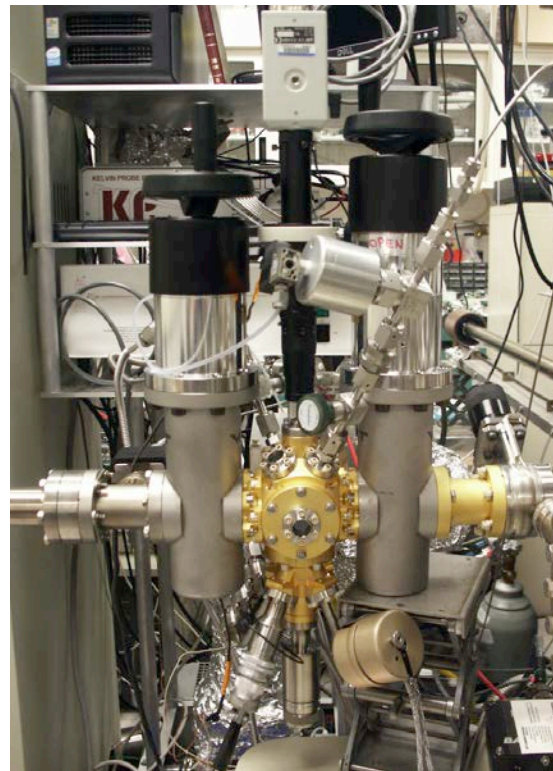
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Summary

- Why
- Experimental issues
- U early stage oxidation
- U early stage hydriding

Slide 1

Why should we use UHV surface science methods to study real world corrosion problems?

- 1) Ability to understand corrosion initiation from a chemical, atomistic, or molecular perspective
- 2) Direct elemental information – first surface phase and impurities
- 3) Chemical state information
- 4) Chemical susceptibility (probability for corrosion to initiate)
- 5) Surface and thin film phase diagrams to describe the metastable surface system when equilibrium thermodynamic phase diagrams don't work

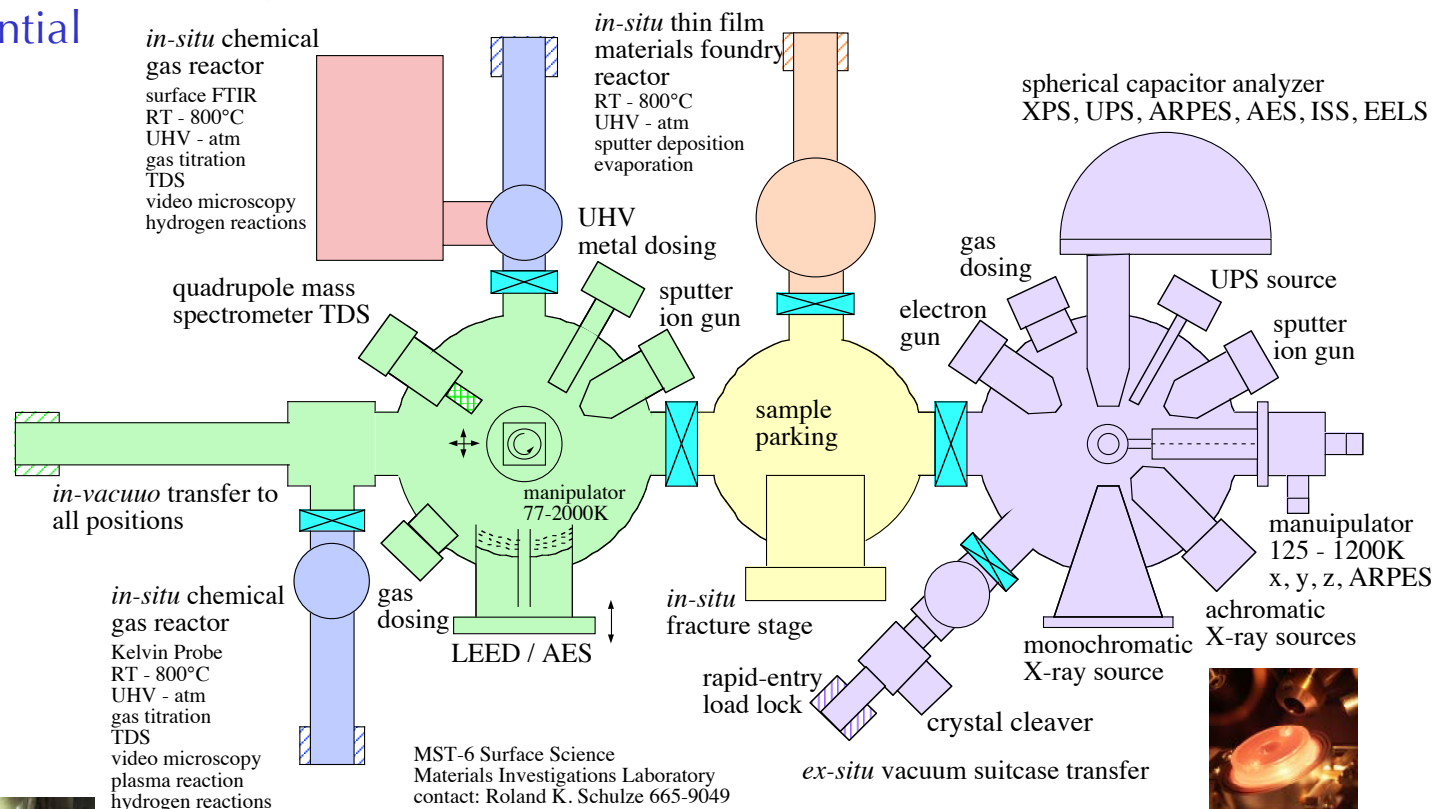
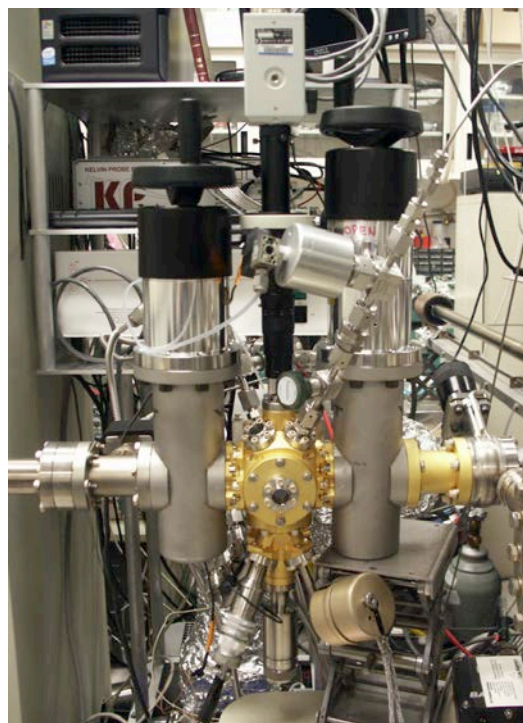
Understanding the early stages of corrosion – initiation

How can we do this – the UHV environment is vastly different than real world engineering conditions?

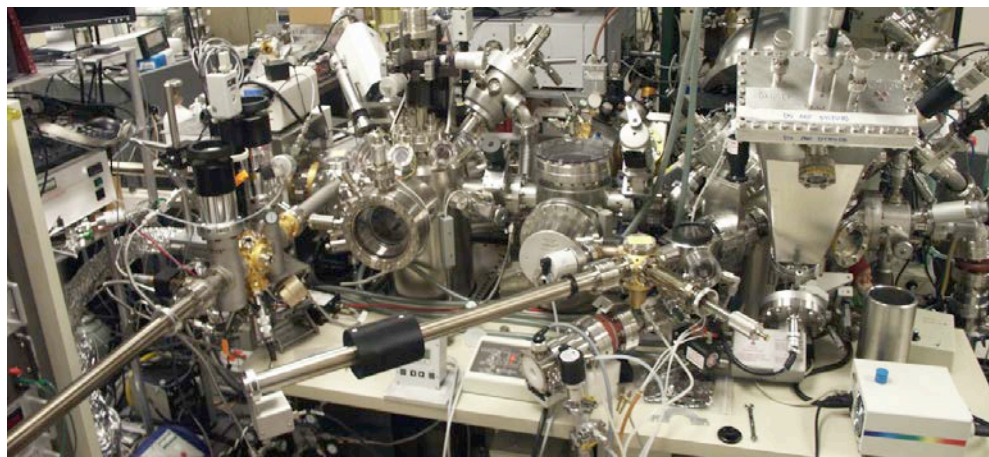
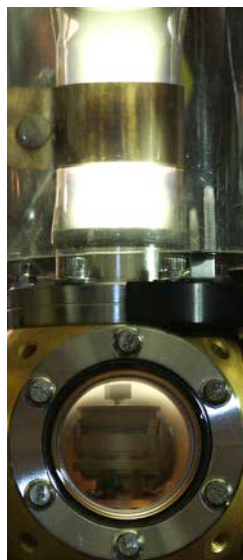
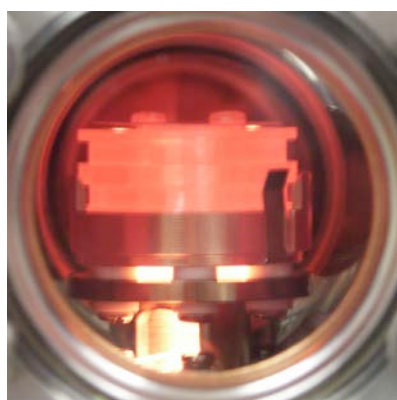
Traditional methods are problematic – process and measurement are decoupled due to atmospheric exposure – need in situ methodology

Methods

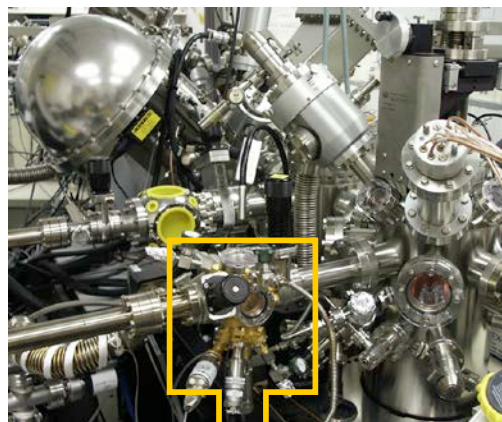
Surface Science / gas-solid reactions / electronic structure / chemical potential



surface chemistry, analytical surface science, electronic structure measurements, single crystal investigations, *in-situ* surface/thin film reactions, materials corrosion, *in-situ* thin film materials synthesis, analytical surface forensics



Surface Science Studies of Uranium-Hydrogen Reactions

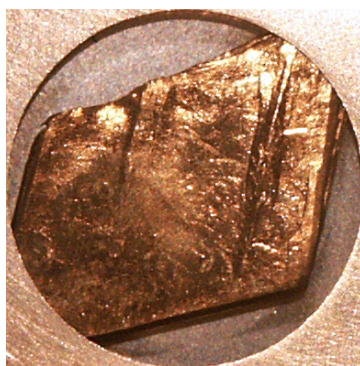


high pressure reactors appended to UHV surface science systems: XPS, UPS, Auger, LEED, EELS, reaction kinetics, TDS, video monitoring

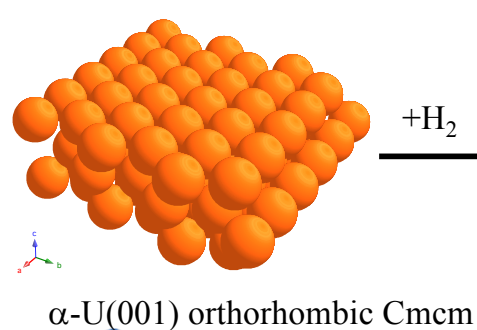
**Reaction Kinetics --
chemical mechanisms
chemical states**



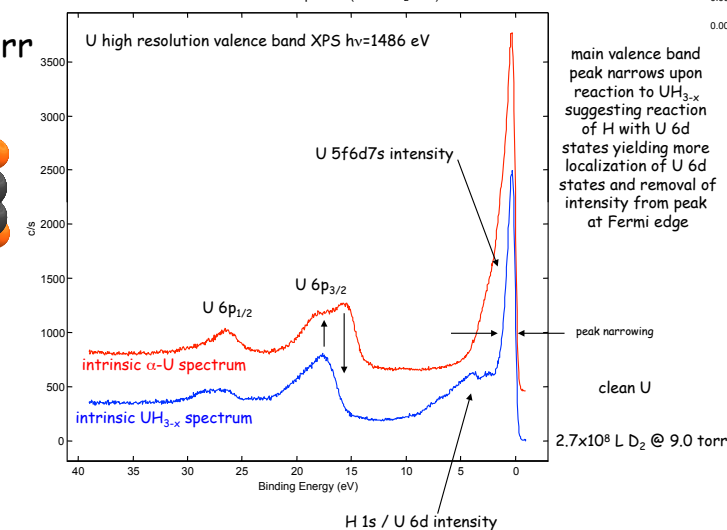
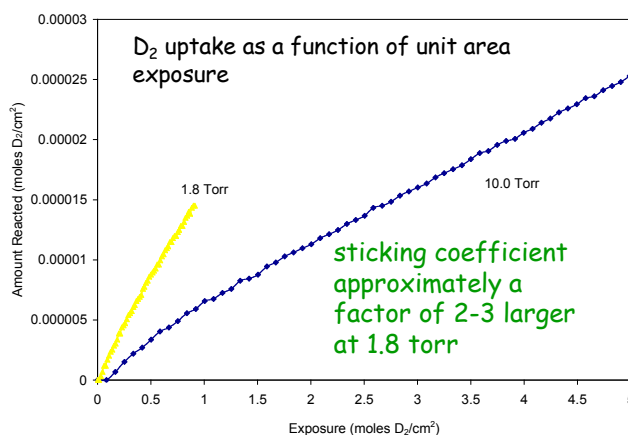
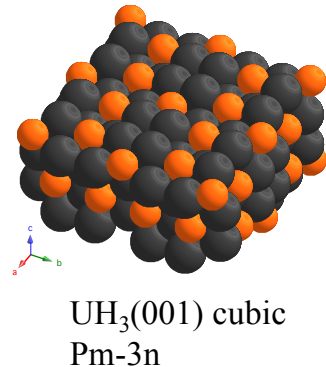
clean U crystal



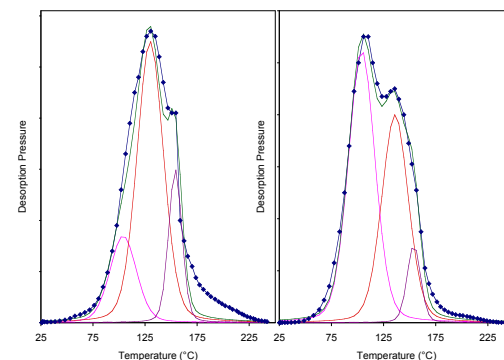
7.4×10^8 L D_2 @ 12.4 Torr



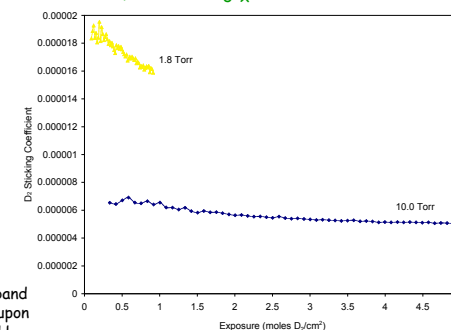
+H₂



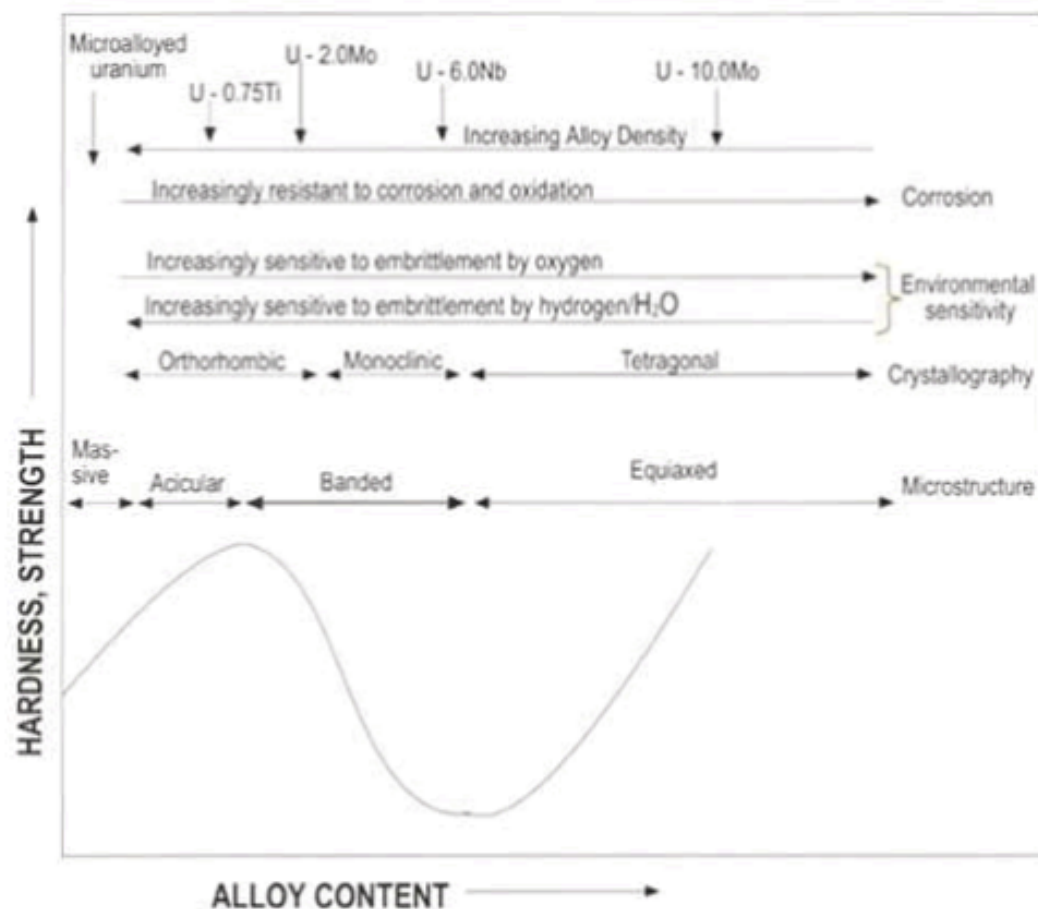
Thermal Desorption measurements



higher D₂ reaction uptake leads to population of different chemical sites--D in solution, UD₃ site nucleation, and UD_{3-x}



Effects of Alloy Composition

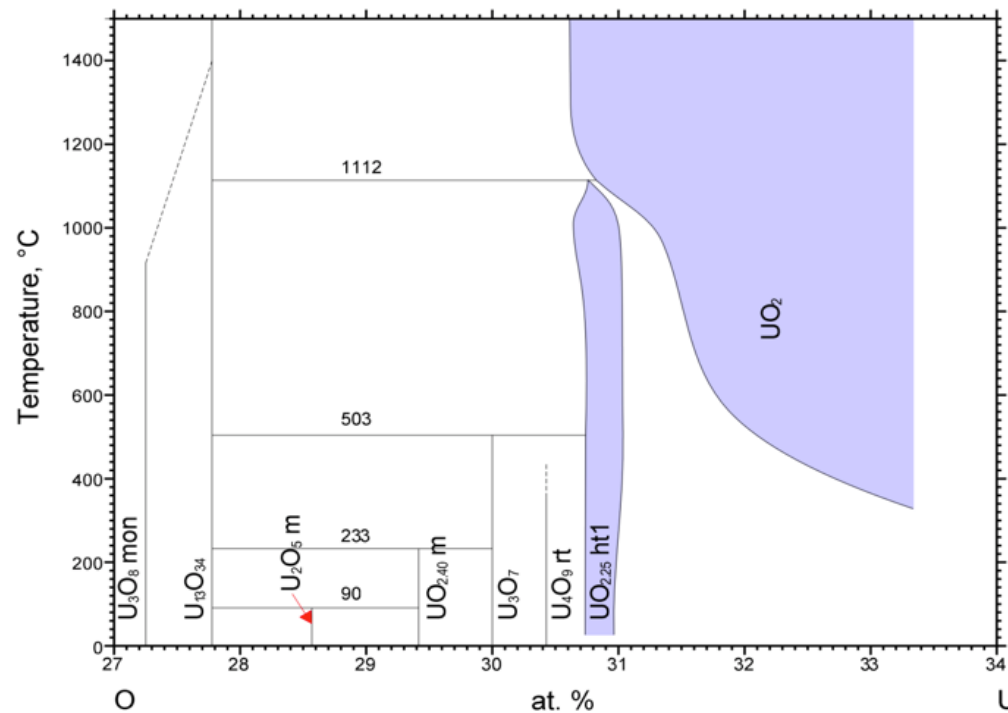


Effects of alloy composition on microstructure, crystal structure, and properties of quenched uranium alloys. (Ref. 1)

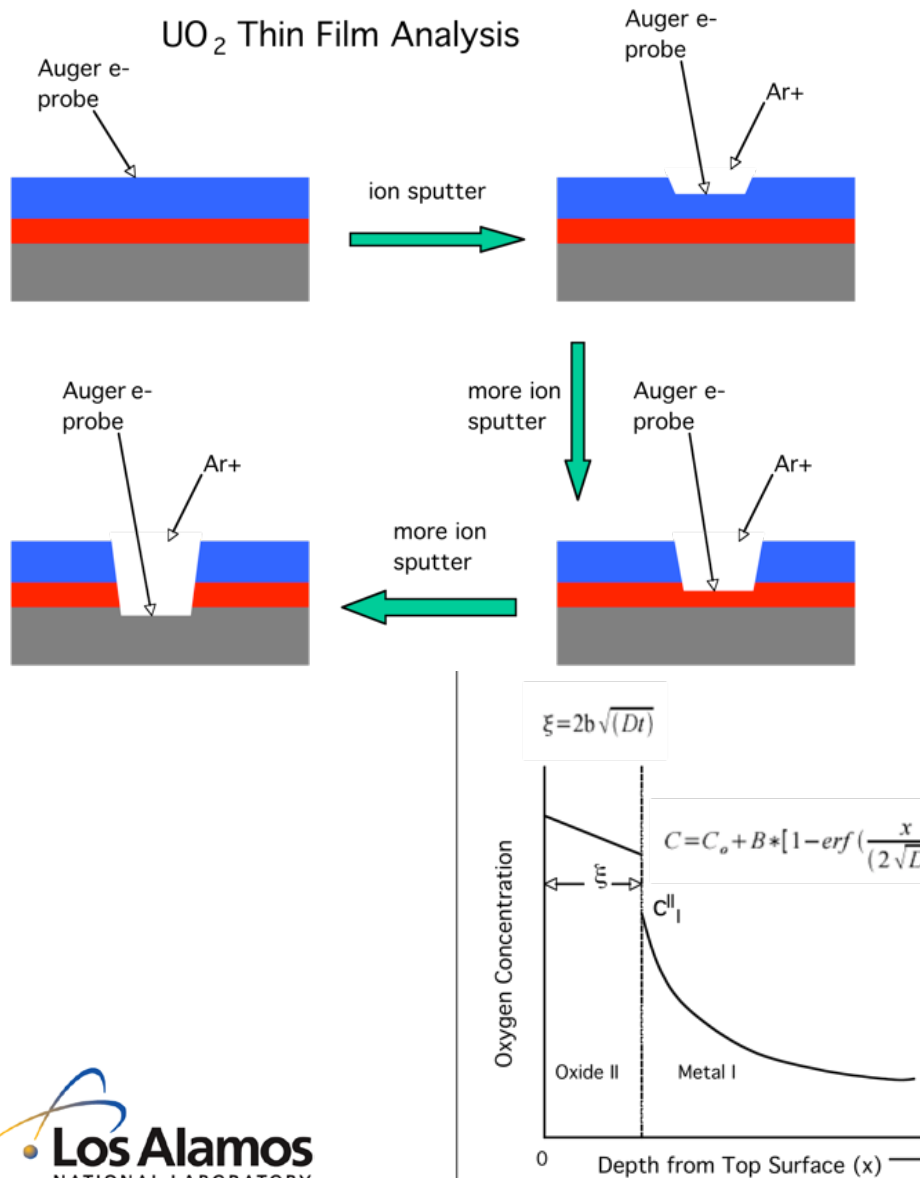
1. Metals Handbook Tenth Edition, Volume 2, Properties and Selection: Nonferrous Alloys and Special Purpose Materials, Uranium and Uranium Alloys, American Society for Metals, Metals Park, OH 44703, 1990, pp. 670 - 682.

Uranium oxidation

- Bulk equilibrium phase diagram for uranium-oxygen system shows many possible stable phases
- Various phases can easily be formed at surfaces in both single crystal UO_2 and thin film $\text{UO}_{2\pm x}/\text{U}$ metal cases
- Broad phase field for UO_2
- Phase stability in thin film oxide case critically determined by headspace conditions, surface chemical potential, and thermal condition
- Dynamic changes in $\text{UO}_{2\pm x}/\text{U}$ case arise from in/out diffusion of $x\text{O}$ depending on headspace chemical potential



Depth profiling to investigate evolution of uranium sub-surface chemical condition with anneal or age (D.P. Johnson and R.K. Schulze)



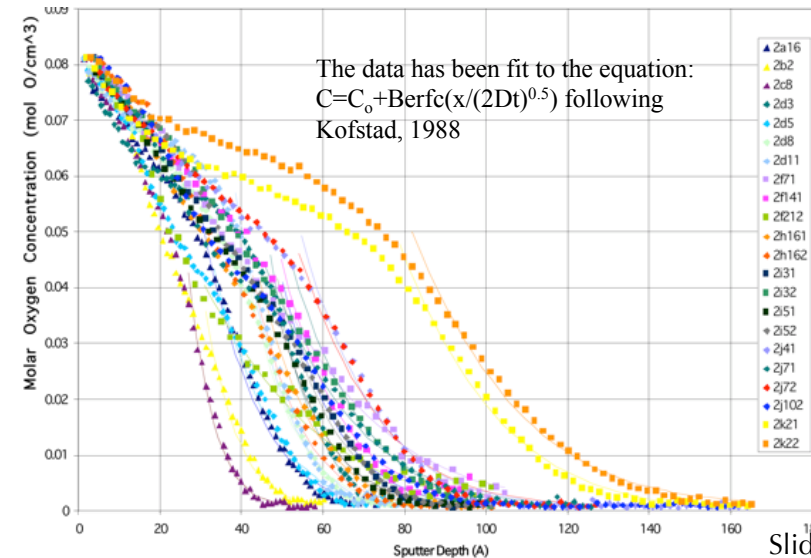
In the general case thick film oxidation follows Fick's laws:

$$dC/dt = Dd^2C/dx^2$$

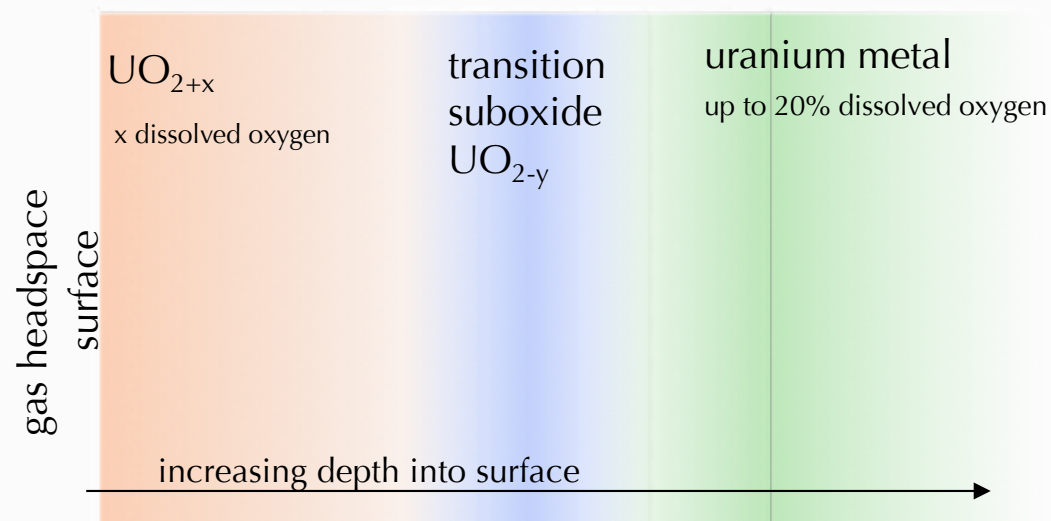
Thin films follow an equation shown by Tu, 1985:

$$\frac{\partial C}{\partial t} = \tilde{D} \frac{\partial^2 C}{\partial x^2} \left(1 + \frac{1}{8} \left(\frac{I f_o}{kT} \frac{\partial C}{\partial x} \right)^2 \right) - \frac{2\tilde{D}}{f_o} K \frac{\partial^4 C}{\partial t^4}$$

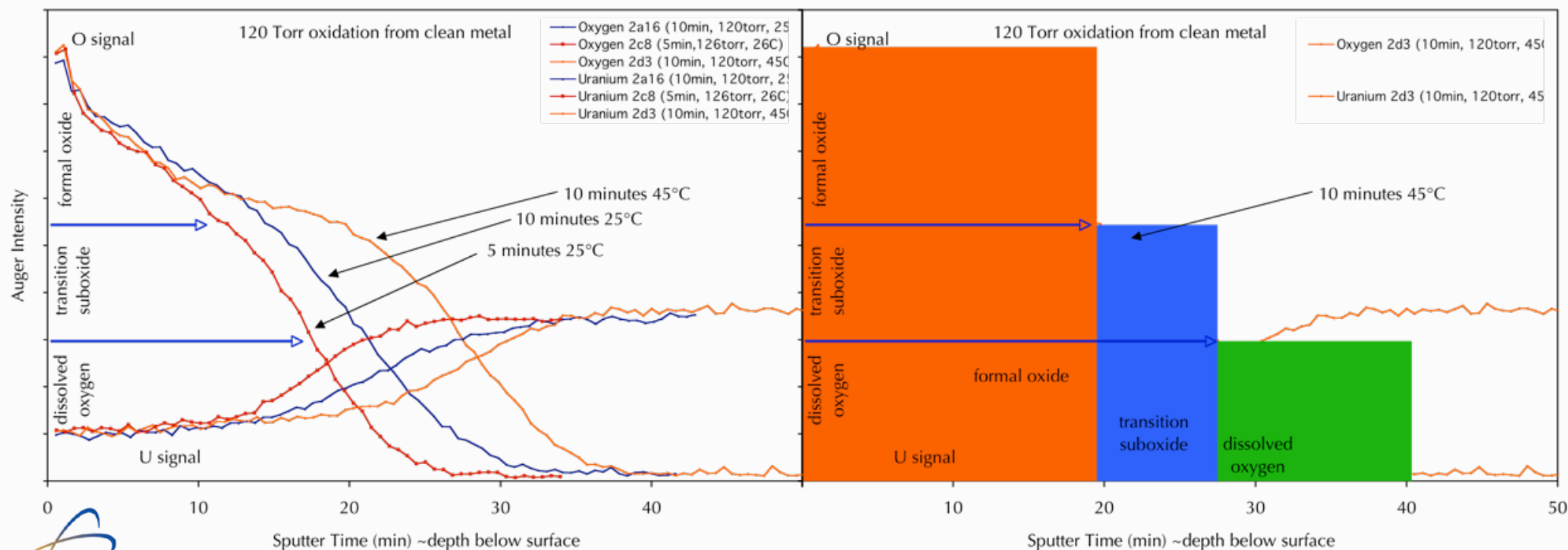
where C is the concentration, x is the position, D is the interdiffusion constant, l is the jump distance, f_o is the second differential of the free energy versus concentration gradient, k is the Boltzmann constant, K is a gradient energy coefficient, and T is temperature in Kelvin (Tu, 1985)



Uranium metal early stage oxidation

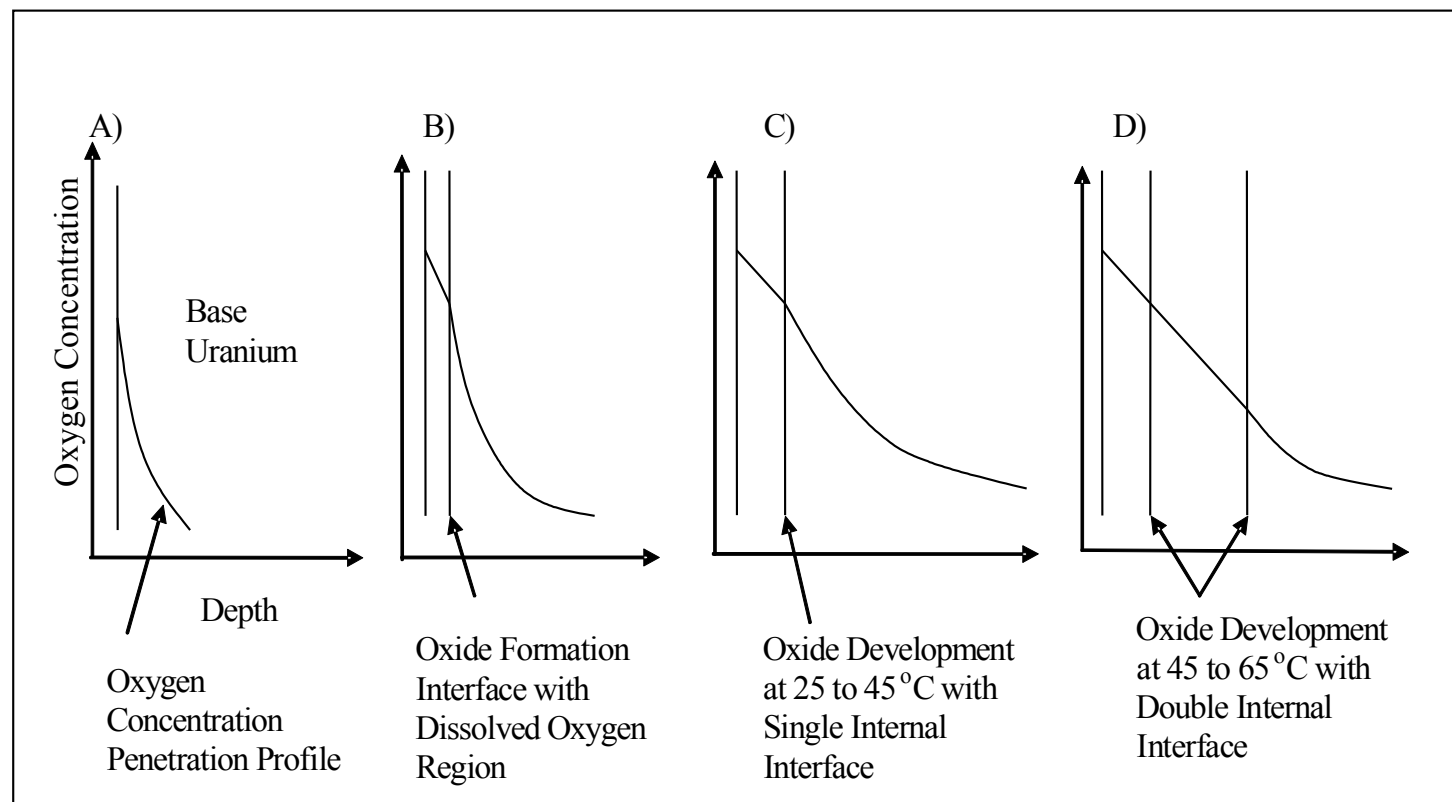


Auger sputter depth profiling



Uranium metal early stage oxidation

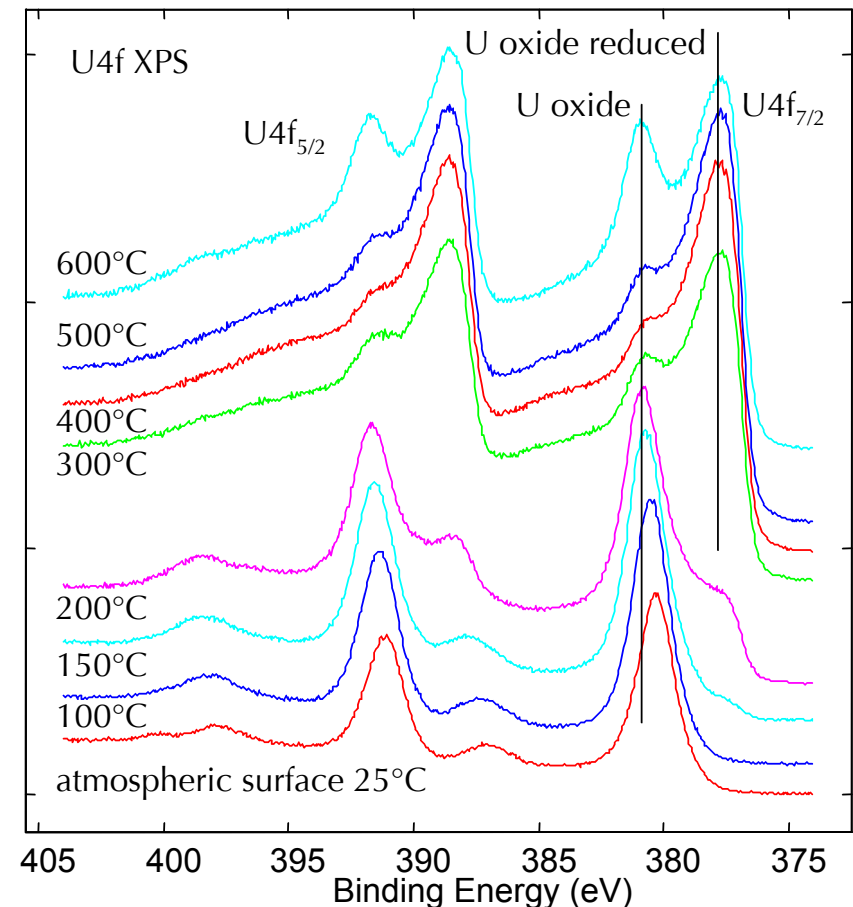
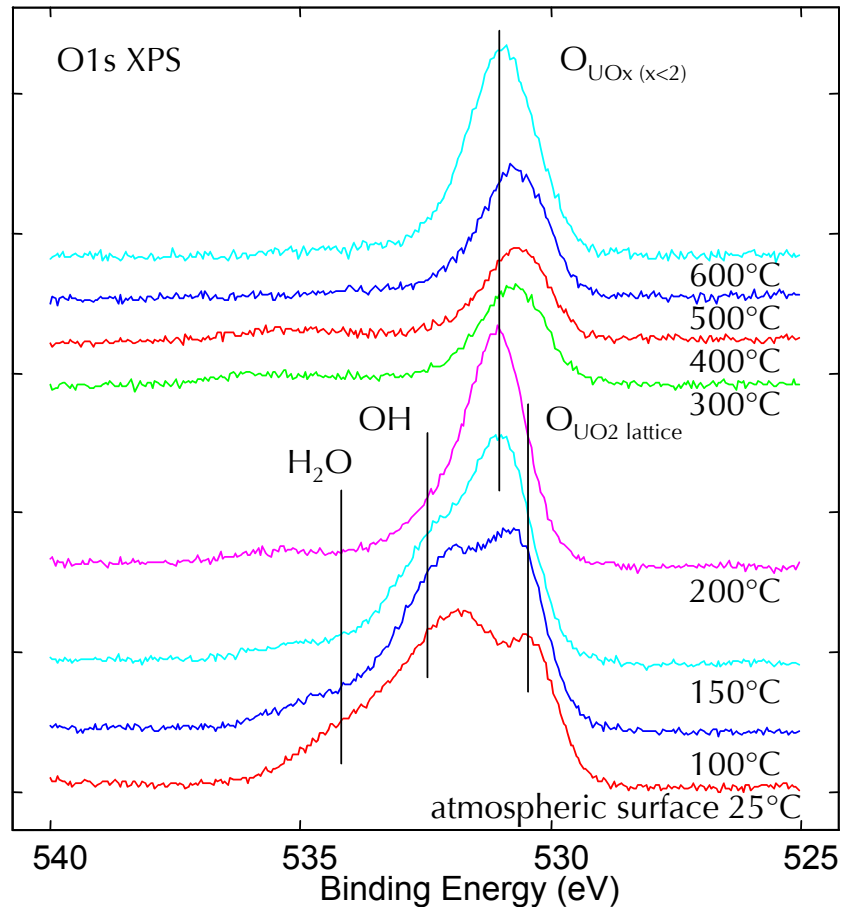
- A) The formation of the oxygen penetration region is shown schematically at early times extending approximately 40 Å deep.
- B) The penetration of the dissolved oxygen into the base uranium continues with time until oxide formation is nucleated forming a layer that is 10 to 20 Å thick.
- C) At later times, both regions of the oxygen penetration (beginning at a concentration of 0.03 to 0.04 mol O/cm³ and spanning a distance of 20 to 70 Å) and the oxide (to an apparent limit of 20 Å) thicken.
- D) At higher temperatures, a second internal interface develops and contributes to the oxide development with the formation of a region that spans a distance of approximately 30 Å with a compositional dependence.



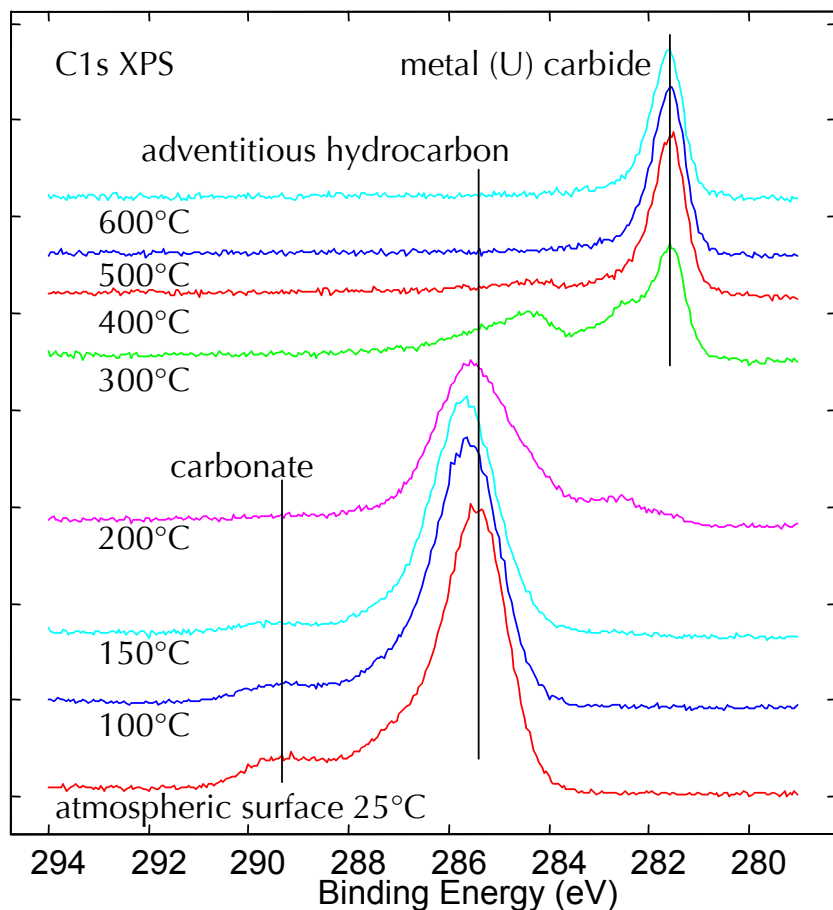
Investigation to understand the early stage oxide formation on uranium under relevant conditions (D.P. Johnson, Colorado School of Mines PhD Thesis, Early Stage Uranium Oxide Development : Kinetic Expressions and Mechanisms, 2007). Oxygen dissolution into the metal was determined to be $D=5.7 \times 10^{-12} e^{(-31000/RT)}$ in cm²/sec with $E_a=30$ kJ/mol for formation of the formal oxide. For a thin oxide film (~100 Å) the surface consists of a thin film of stoichiometric UO₂ overlaying a transition suboxide of substantial thickness. There is also oxygen dissolved into the metal subsurface at high levels of 20 to ~0.1 atomic percent creating a reactive subsurface. Heating of this surface in a reducing environment deoxygenates the film with the excess oxygen being driven further into the subsurface.

The reactivity of an engineering-like (air exposed) uranium surface towards hydrogen increases following a vacuum anneal -- “accelerated aging”

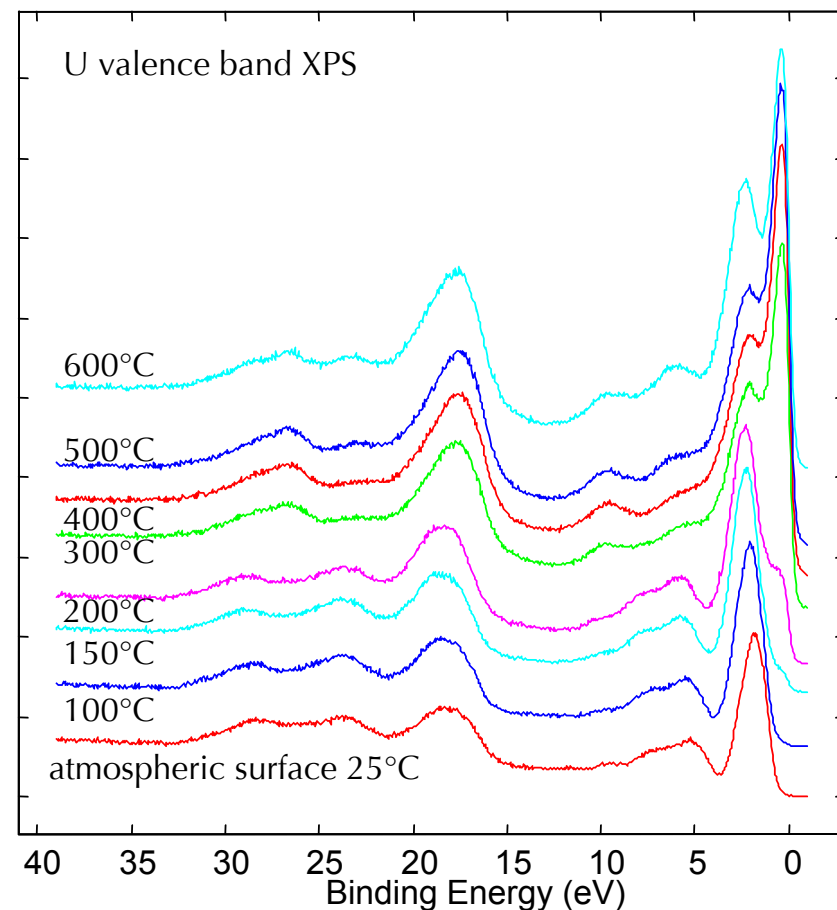
- Careful X-ray photoelectron spectroscopy study
- How does the surface chemistry change with this vacuum anneal?
- Might this also happen at room temperature in an inert or reducing environment?



- Removal of adsorbed water with vacuum anneal
- Removal of hydroxyl groups with vacuum anneal
- Deoxygenation of UO_2 lattice at higher temperature



- Removal of surface carbonate groups
- Removal of adventitious surface hydrocarbon
- Reaction of surface hydrocarbon with metal to produce carbide material at higher temperatures



- UO_2 becomes reduced with vacuum anneal
- Surface shows metallic or metallic-like state suggesting greater conductivity, defect states, and probably higher reactivity and transport behavior

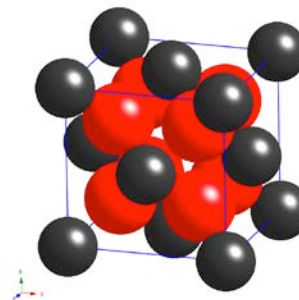
- Removal of adsorbed water with vacuum anneal
- Removal of hydroxyl groups with vacuum anneal
- Deoxygenation of UO_2 lattice at higher temperature

Thermal treatment of an engineering-like (air exposed) uranium surface
in a hard vacuum ($<1 \times 10^{-8}$ Torr) -- "accelerated aging"

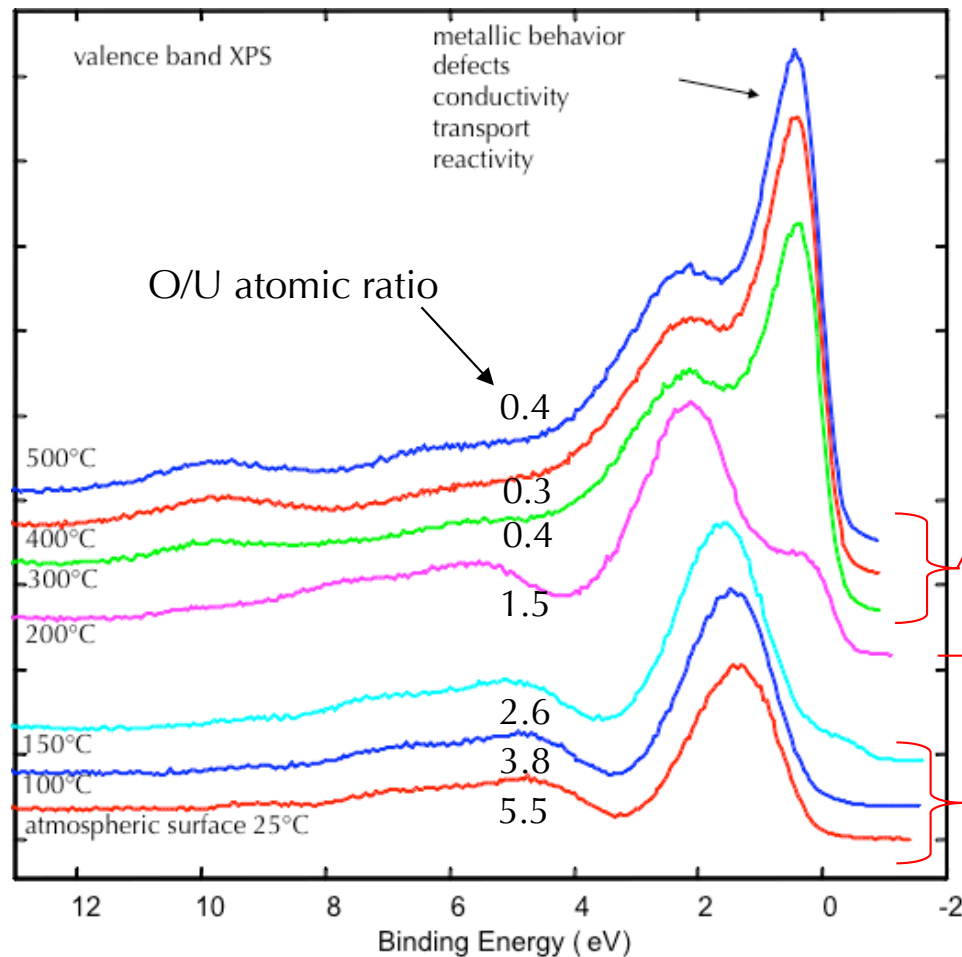
XPS Data -- electronic valence band

valence band spectroscopy of thin film structure very important

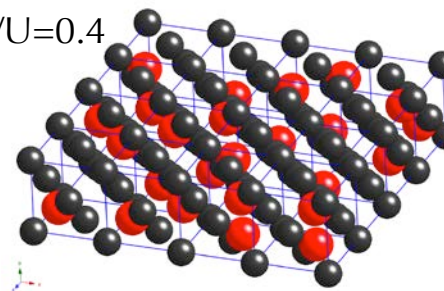
---> atomistic/molecular chemical behavior of surface



UO₂ cubic fluorite

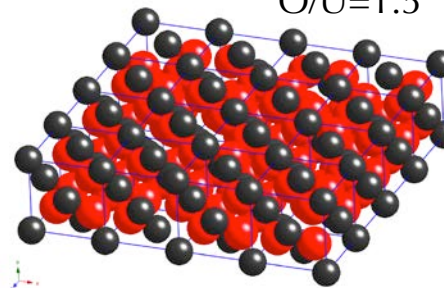


O/U=0.4



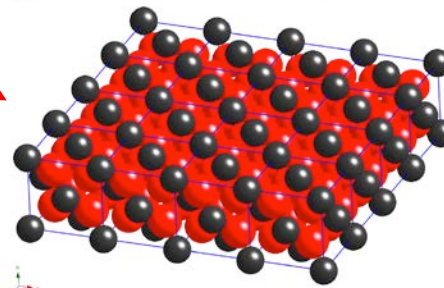
Heavily reduced oxide
most likely leading to
restructure and local
non-equilibrium defect
phases -- 80% of
oxygen atoms removed

O/U=1.5



Mildly reduced oxide
with oxygen vacancies
-- defect structure 25%
of oxygen atoms
removed

O/U=2.0



Coherent or near-
coherent oxide

Summary of surface behavior of $\text{UO}_2(\text{OH})_x(\text{H}_2\text{O})_y$ / UO_2 / U with vacuum anneal to equilibrium conditions (situation analogous to inert environment)

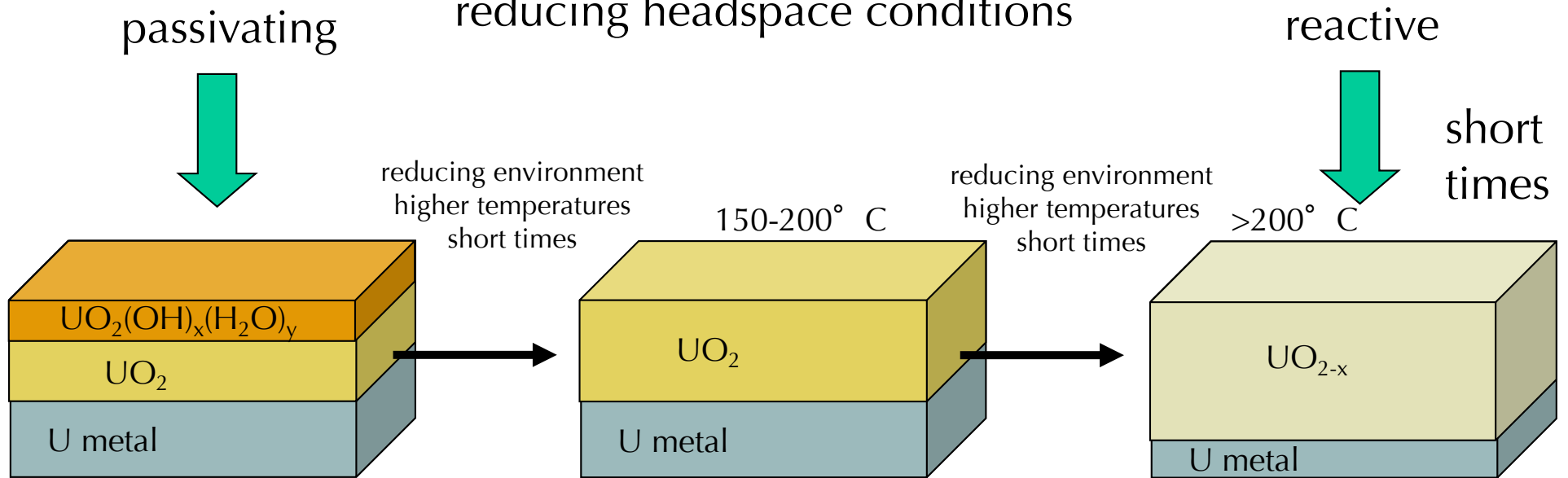
temperature	surface condition
25° C	native oxide UO_2 , partially hydroxylated, adsorbed water, hydrocarbon, top surface carbonate, insulator (small band gap)
100° C	mildly dehydrated, mildly dehydroxylated
150° C	dehydrated, much of hydroxyl removed, UO_2 is mildly deoxygenated
200° C	hydroxyl removed, surface carbonate removed, UO_2 is partially reduced
300° C	carbide/oxycarbide begins to form, UO_2 strongly reduced, metallic behavior in VB (intensity at Fermi edge)
400° C	carbide/oxycarbide, UO_{2-x} (protective oxide reduced), strong defect behavior in VB
500° C	carbide/oxycarbide persistent, UO_{2-x} persistent, strong defect behavior in VB
600° C	carbide/oxycarbide persistent, UO_{2-x} persistent, strong defect behavior in VB

Uranium thin film surface structure reactivity with hydrogen at various temperatures - qualitative observations

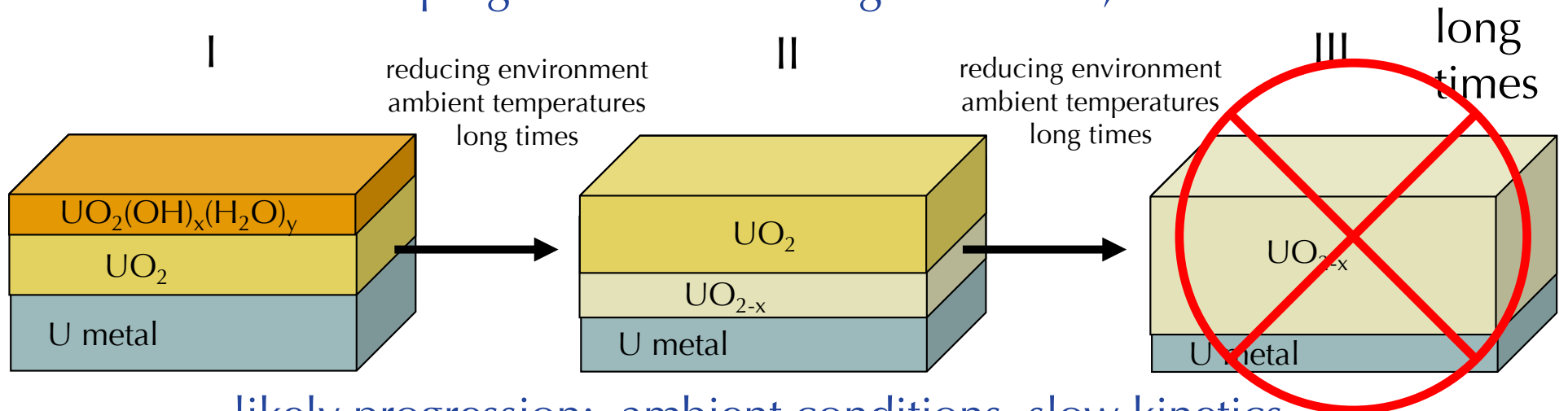
Issues:

- State of the surface -- annealing / exposure history
- Changes in the oxide layer
 - Annealing in reducing environment
 - Long term exposure to reducing environment at ambient temperatures
- Induction period
- Subsurface nucleation phenomenon
- Transport of reactive species through oxide layer

Thin film evolution surface models for reducing headspace conditions



measured progression: annealing conditions, fast kinetics



likely progression: ambient conditions, slow kinetics

very slow

general behavior	specific characteristics
Regime I -- passivating ambient	oxide layer maintained in oxidizing environment coherent UO_2 , partial hydroxylation, atmosphere exposed delivery and transport controls reaction short circuit passivation through defects in oxide subsurface nucleation catastrophic failure due to pitting corrosion fostered by deformation strain in material (Tanski model)
Regime II -- passivating? annealed or reducing conditions	oxide layer coherent but dehydrated For heated systems oxide layer may have annealed character reaction details yet indeterminate
Regime III -- reactive annealed or reducing conditions	oxide layer deoxygenated and possibly thinned defected nature of oxide yields rapid transport and overall reaction direct reaction suspected

Evolution of Reactive States of UO_2 thin films: oxide film phase diagram

- Surface and thin film situation is inherently non-equilibrium
- Conventional analysis by equilibrium phase diagrams DO NOT work
- Reactivity prediction by gas and surface chemical potential (Kelvin probe measurements)

Determination of Reactivity Threshold levels based on System Thermodynamics and Surface Chemical Potential

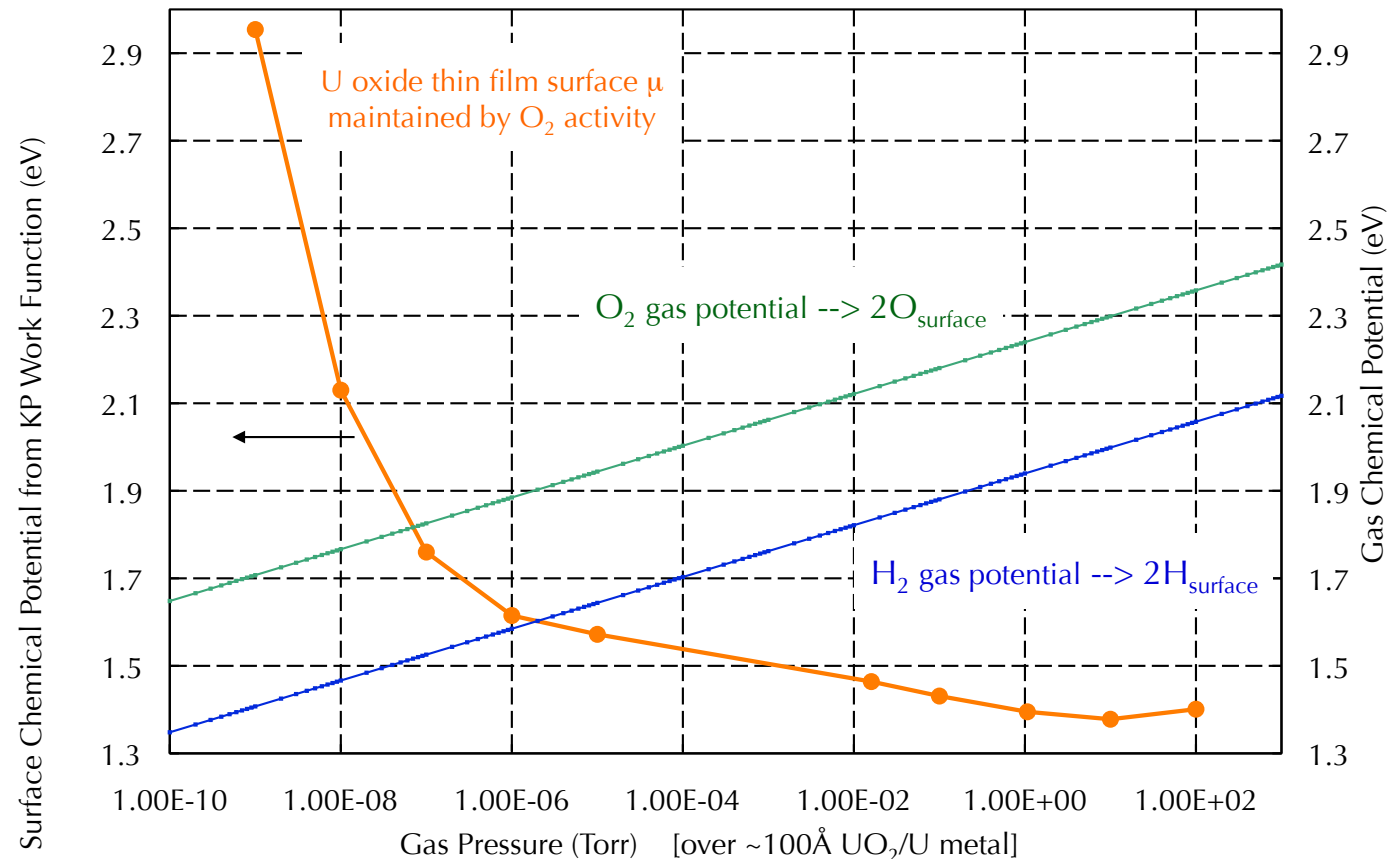
Surface $e\Phi = D + (-\mu_{\text{Fermi}})$

Gas $\mu_{\text{@Fermi}} = \mu^0 + kT \ln(p/p^0)$

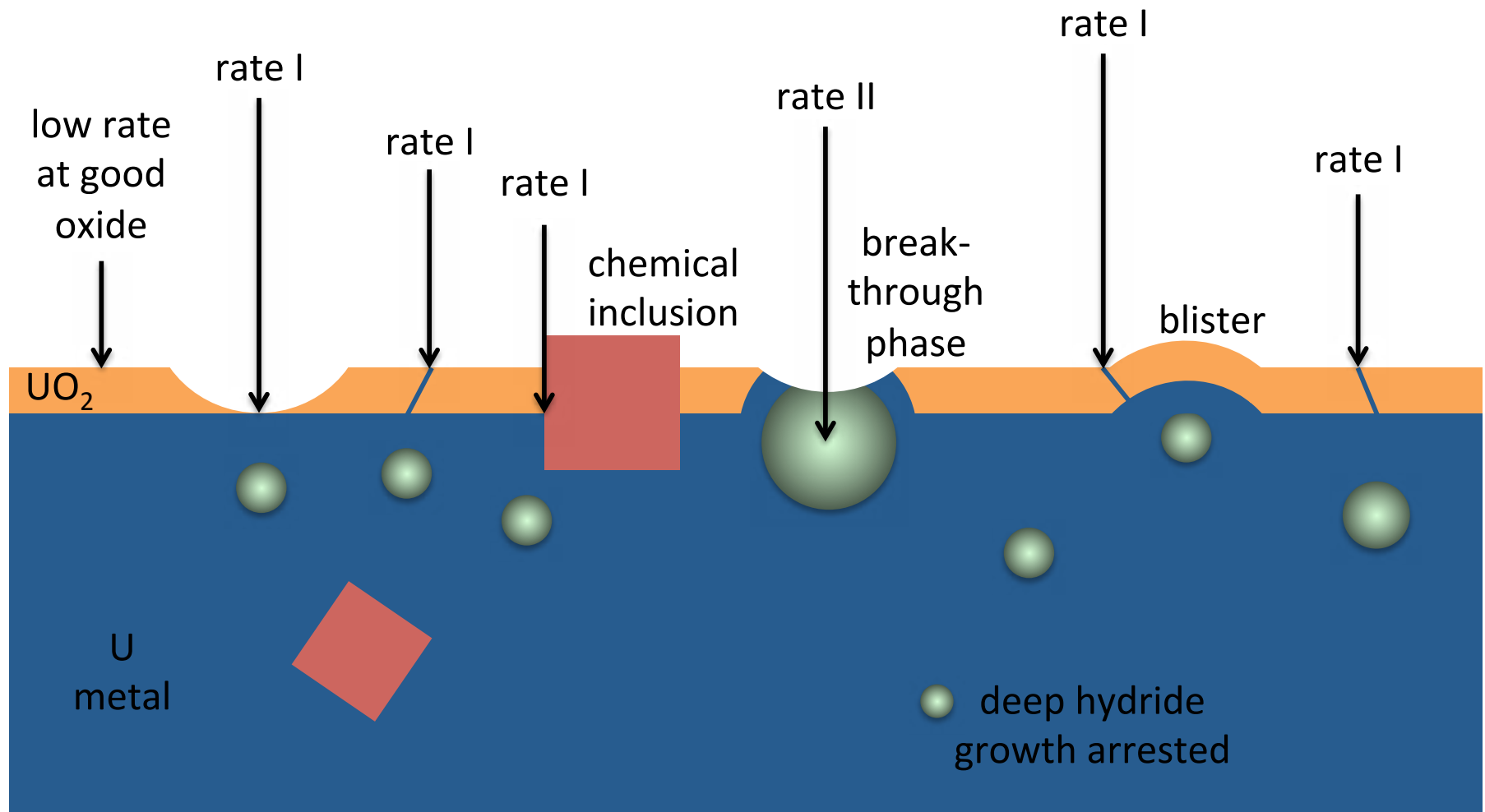
H_2 gas potential $\rightarrow 2\text{H}_{\text{@Fermi}}$

If μ of the gas phase exceeds μ in the solid then reaction occurs (transport and or chemical transformation)

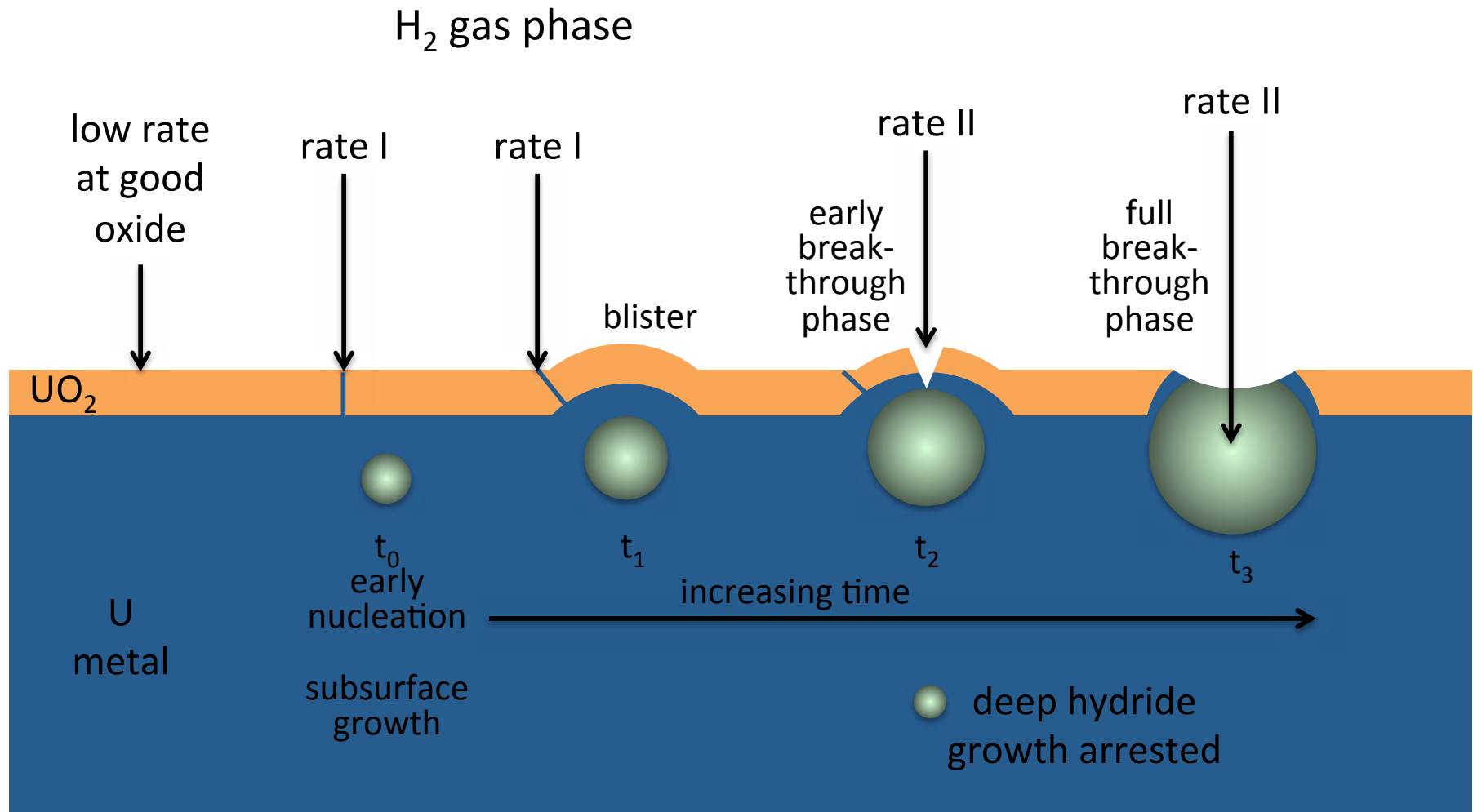
For gas pressure $> \sim 1 \times 10^{-6}$ torr H_2 reaction occurs - at lower pressures passivity is maintained as long as oxidizer is present at sufficient activity



Uranium hydriding corrosion – early stage molecular → mesoscopic → microscopic → mm-size



Uranium hydriding corrosion – early stage molecular \rightarrow mesoscopic \rightarrow microscopic \rightarrow mm-size



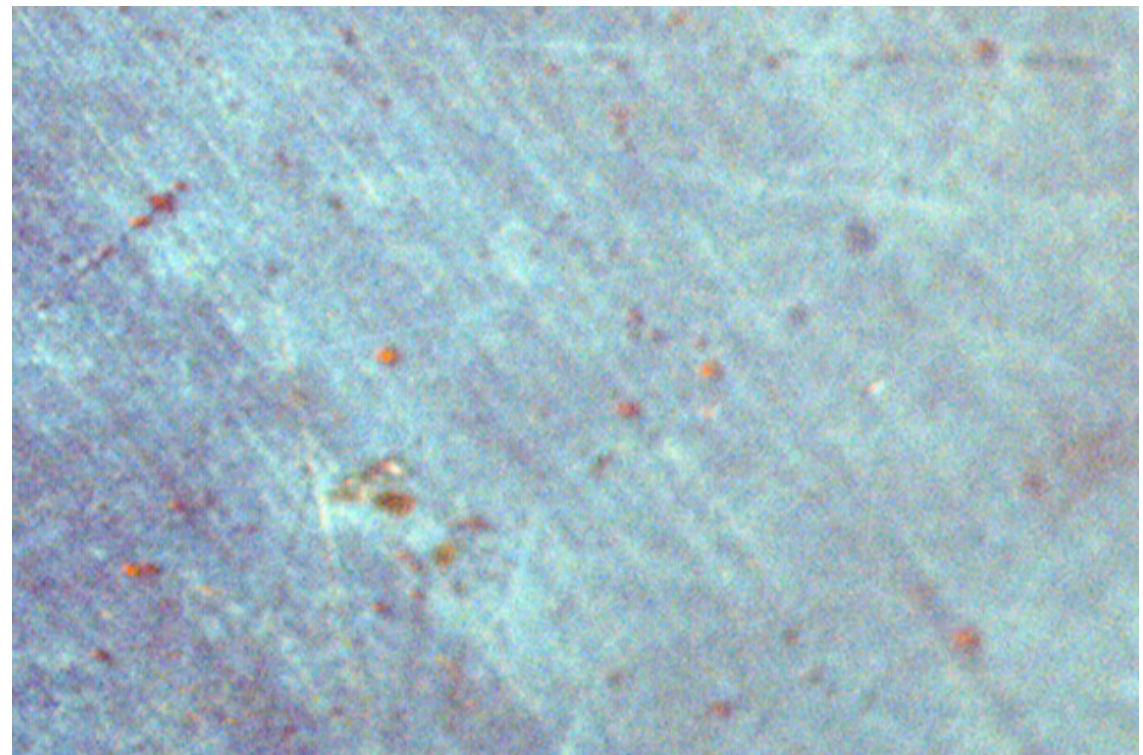
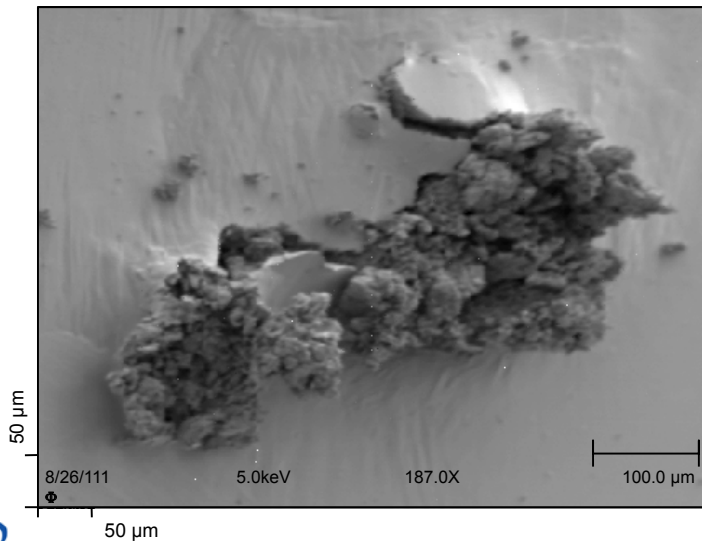
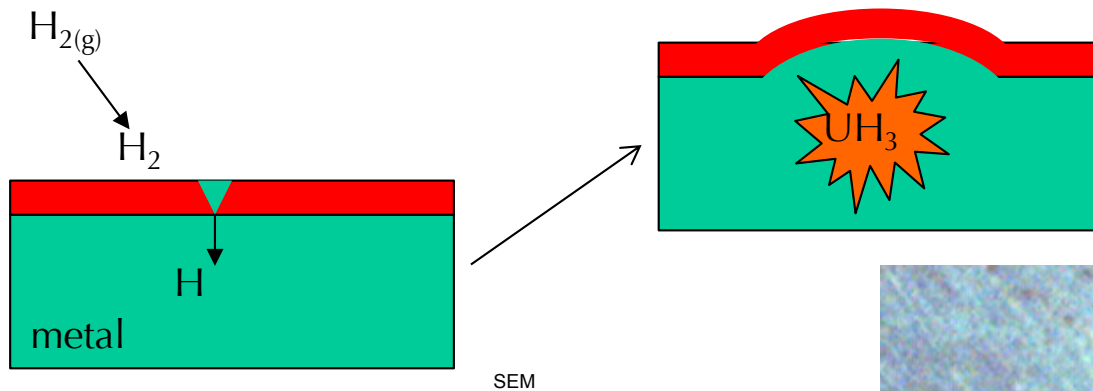
Careful understanding of the surface condition (defected oxide) using integrated surface science methods has allowed us to understand mechanistically the hydride corrosion behavior at early stage for uranium metal surfaces

- 1) Delivery of hydrogen gas to the surface
- 2) Adsorption of molecular hydrogen on the oxide and dissociation into atomic hydrogen
- 3) Transport of atomic hydrogen through a defect in the oxide layer (transport slow through coherent, perfect UO_2) - the defect can be a void or crack in the oxide, oxide grain boundary, chemical base metal inclusion disrupting the coherency of the oxide film, partial chemical reduction of a location of oxide (e.g. reduction by hydrocarbons), or mechanical abrasion/disruption of oxide film
- 4) Dissolution of atomic hydrogen into metal subsurface (below oxide metal interface)
- 5) Transport in metal to nucleation site (unknown but perhaps preexisting hydride nuclei) or supersaturation leading to spontaneous nucleation
- 6) Growth of UH_3 hydride nucleus with corresponding volume expansion
- 7) Volume expansion of metal atom density leads to buried blistering at surface (detectable by SEM imaging and probably other methods such as SPM)
- 8) Yield strength of actinide metal above blister exceeded leading to blister rupture at surface and breakthrough phase of corrosion
- 9) Delivery of hydrogen gas to hydride breakthrough site now fully efficient and rapid – volume of hydride grows at bulk kinetic rate consuming underlying metal
- 10) Hydride product spalls as volume increases leading to pitting corrosion phenomenon

Key to this was understanding the chemical and morphological nature of the thin film oxide

Hydriding Mechanism for (oxide covered) Uranium Surfaces

- Induction period (gas delivery, transport thru defect, dissolution into metal subsurface, nucleation and growth of UH_3 hydride nucleus) – induction time may be determined by many factors (state of oxide, nature of defects, etc.)
- Blistering due to UH_3 volume expansion in metal subsurface
- Breakthrough phase – growth follows Condon-Kirkpatrick bulk kinetics



Uranium Hydriding Mechanism for Real World Surface

The mechanism for hydriding at surfaces is as follows:

- 1) Delivery of hydrogen gas to the surface
- 2) Adsorption of molecular hydrogen on the oxide surface (and dissociation into atomic hydrogen)
- 3) Transport of atomic hydrogen through a defect in the oxide layer (transport is very slow through coherent, perfect UO_2). The defect can be a void or crack in the oxide, oxide grain boundary, chemical base metal inclusion disrupting the coherency of the oxide film, partial chemical reduction of a location of oxide (e.g. reduction by hydrocarbons), or mechanical abrasion/disruption of oxide film.
- 4) Dissolution of atomic hydrogen into metal subsurface (below oxide metal interface)
- 5) Transport in metal to nucleation site (unknown) or supersaturation leading to spontaneous nucleation
- 6) Growth of actinide hydride nucleus (UH_3) with corresponding volume expansion
- 7) Volume expansion of metal atom density leads to buried blistering at surface (detectable by microscopy)
- 8) Yield strength of actinide metal above blister exceeded leading to blister rupture at surface and breakthrough phase of corrosion
- 9) Delivery of hydrogen gas to hydride breakthrough site now fully efficient and rapid (Condon Kirkpatrick kinetics)– volume of hydride grows at bulk kinetic rate consuming underlying metal
- 10) Hydride product spalls as volume increases leading to pitting corrosion phenomenon

Pitting corrosion is frequently referred to as “stochastic”. What this really means is that the factors leading to this type of corrosion are not understood and the location of the corrosion is not predictable. This is the case here, where steps 3 and 5 are not predictable or well understood

Uranium Hydriding Mechanism for Real World Surface

The mechanism for hydriding at engineering surfaces is as follows:

- 1) Delivery of hydrogen gas to the surface
- 2) Adsorption of molecular hydrogen on the oxide surface
- 3) Transport of atomic hydrogen through a defect in the oxide layer
- 4) Dissolution of atomic hydrogen into metal subsurface (below oxide metal interface)
- 5) Transport in metal to nucleation site (unknown) or supersaturation leading to spontaneous nucleation
- 6) Growth of actinide hydride nucleus (UH_3) with corresponding volume expansion
- 7) Volume expansion of metal atom density leads to buried blistering at surface
- 8) Blister rupture at surface and breakthrough phase of corrosion
- 9) Delivery of hydrogen gas to hydride breakthrough site now fully efficient and rapid (Condon Kirkpatrick kinetics)– volume of hydride grows at bulk kinetic rate consuming underlying metal
- 10) Hydride product spalls as volume increases leading to pitting corrosion phenomenon

Steps 1-7 are the induction period prior to hydride detection

Steps 8-10 are past the detectable breakthrough phase and grow at bulk kinetic rate

Uranium Hydriding Mechanism

1) Hydrogen gas delivery to surface

Flux (molecules/cm²sec)

$$f = \frac{P}{\sqrt{2\pi MRT}}$$

P = gas pressure

M = gas molar mass

R = ideal gas constant =
 $k_B \cdot 6.022 \times 10^{23}$

T = gas temperature

For H₂ gas at 25° C and a surface
 with 1×10^{15} atoms/cm²

Gas pressure (torr)	Flux of molecules f (H ₂ /cm ² sec)	Monolayer time (sec)	Mean free path λ (cm)
liquid		$\sim 10^{-12}$	$\sim 10^{-8}$
1000 atm	1.1×10^{27}	$\sim 10^{-12}$	$\sim 10^{-8}$
760	1.1×10^{24}	9.1×10^{-10}	1.1×10^{-5}
100	1.4×10^{23}	7.0×10^{-9}	8.1×10^{-5}
10	1.4×10^{22}	7.0×10^{-8}	8.1×10^{-4}
1	1.4×10^{21}	7.0×10^{-7}	8.1×10^{-3}
0.1	1.4×10^{20}	7 μ sec	8.1×10^{-2}
0.01	1.4×10^{19}	7.0×10^{-5}	8.1×10^{-1}
1 mtorr	1.4×10^{18}	7.0×10^{-4}	8.1
1×10^{-4}	1.4×10^{17}	7 msec	81
1×10^{-5}	1.4×10^{16}	0.07	810
1×10^{-6}	1.4×10^{15}	0.7	8100

Uranium Hydriding Mechanism

2) Adsorption onto surface

Adsorption isotherms

θ = fractional coverage

$$K = 10^6 \cdot s_o \tau_d$$

Simple physisorption yields
Langmuir isotherm if $s = s_o(1 - \theta)$

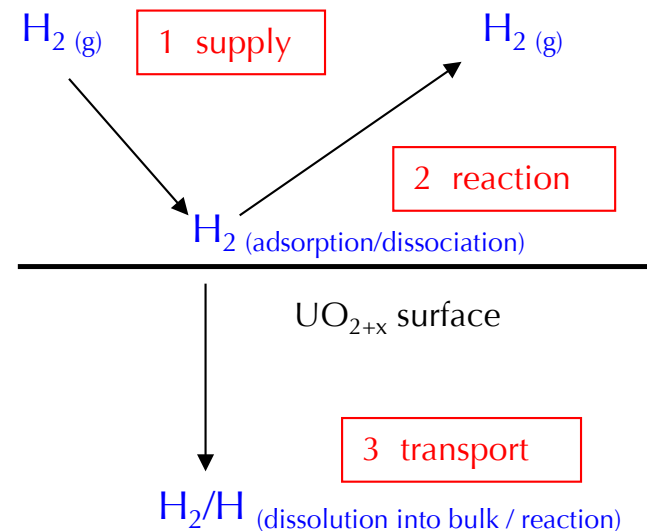
$$\theta = \frac{KP}{1 + KP}$$

If a reaction removes H_2 from the surface (dissociation, diffusion into bulk) and possibly frees up a sticking location, then the reaction rate r_R

$$r_R = k_R n_{H_2(s)} \theta = \frac{k_R n_{H_2(s)} KP}{1 + KP}$$

sticking coefficient is the fraction of molecules that adsorbing (irreversibly – or reacting) relative to the total surface flux

s is likely to be very small on “good” U oxide thin film surfaces



Uranium Hydriding Mechanism

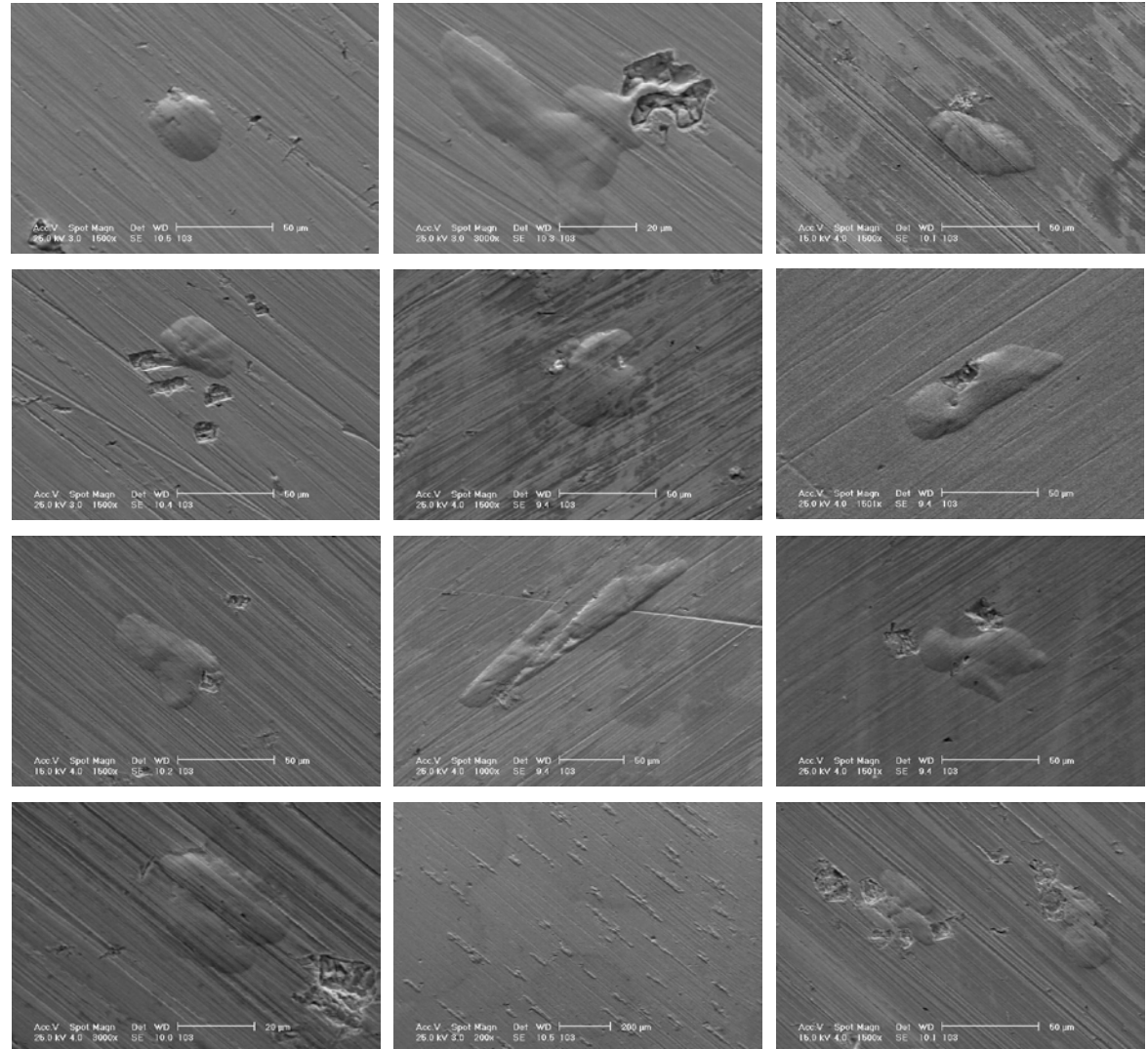
3) Transport of hydrogen through oxide layer

hydride blister formation always near surface defect

Because hydrogen transport through “good” UO_2 oxide is believed to be quite slow,
Transport of hydrogen in crystalline UO_2
 $D = @298\text{K } D = 10^{-12} - 10^{-13} \text{ cm}^2/\text{sec}$

most of the hydrogen that gets into the metal subsurface is “short circuited” through defects in the oxide:

- Oxide pinholes
- Fractured oxide
- Abraded oxide spots
- Chemical inclusions from base metal
- Oxide grain boundaries
- Reduced (substoichiometric) oxide
 - Thermal
 - Hydrocarbon
- Incomplete oxide from high energy features
 - Edges / corners
 - Surface base metal voids
 - Surface base metal cracks



Uranium with “good coherent” oxide is very resistant to hydriding
e.g. very clean annealed metal with O_2 grown oxide, electropolished metal

Uranium Hydriding Mechanism

4) Dissolution of hydrogen into metal subsurface

5) Transport of hydrogen in metal to nucleation site

Transport of hydrogen in α -U metal

$$D = 0.019 \exp(-46320/RT) \text{ cm}^2/\text{sec}$$

$$R = 8.314 \text{ J/Kmol}$$

$$\text{@298K } D = 1.4 \times 10^{-10} \text{ cm}^2/\text{sec}$$

In comparison,

Transport of hydrogen in UO_2 crystal

$$D = \text{@298K } D = 10^{-12} - 10^{-13} \text{ cm}^2/\text{sec}$$

Hydride nucleation which leads to corrosive hydride pitting has been shown to occur at subsurface locations and NOT at the oxide – metal interface

Probably only the nucleation which occurs within the top few 10s of μm leads to pitting corrosion

- The deeper the nucleation site the lower the H_2 delivery rate
- Deeper nucleation sites will stop growing from compressive strain of the surrounding metal

What are the nucleation sites?

- Preexisting hydrides (Siekhaus, Balusubmaranian)
- Chemical impurities (Hanrahan, Hill, Schulze)
- Low activation energy for absorption / reaction to UH_x

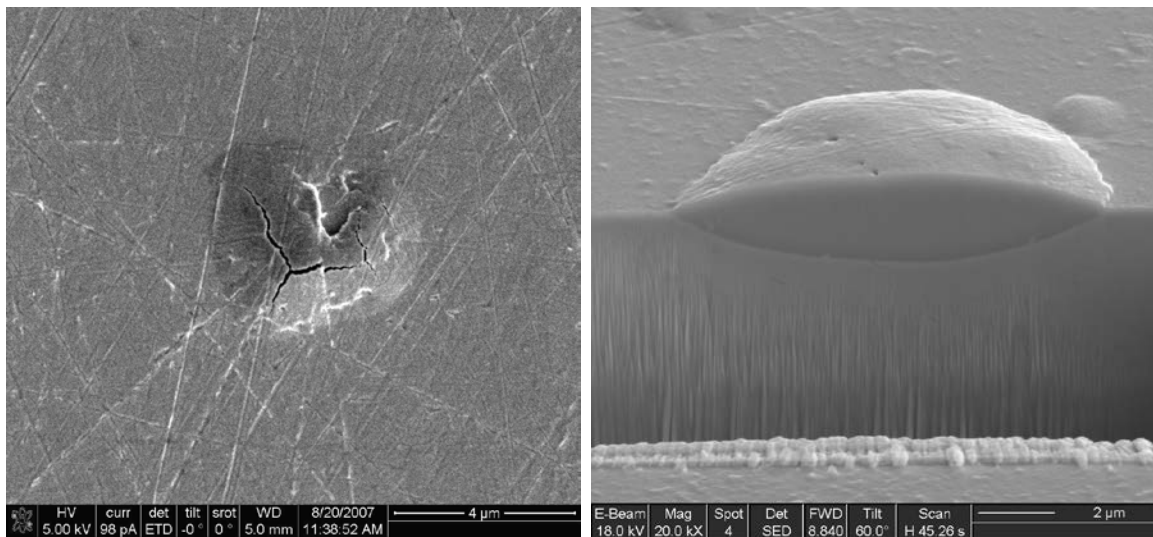
Remember: 1 ppmw of H in U is 238 ppm atomic

Possibly up to 2000-3000 ppm atomic trapped in U metal depending on casting and processing conditions

Uranium Hydriding Mechanism

7) Volume expansion of hydride UH_3

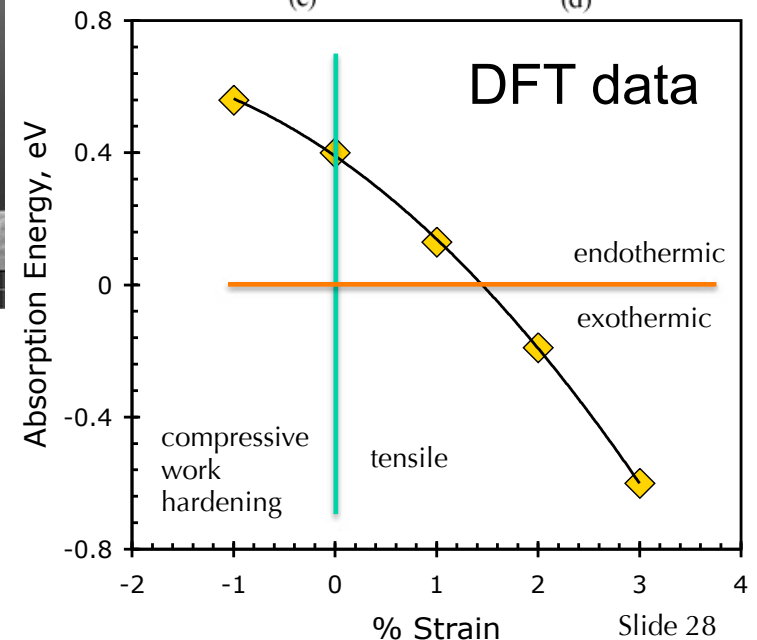
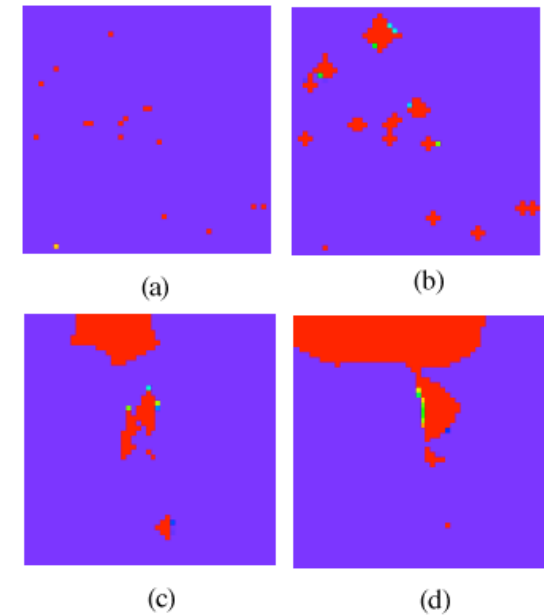
- Uranium hydride pits starts as a sub-surface nucleation and growth process
- Nucleation occurs on inhomogeneous sites in the metal matrix, which appear most consistent with the segregation of impurities
- Predicts nucleation and growth kinetics qualitatively similar to those observed experimentally



$\alpha\text{-U}$ 19.1 g/cm³ 80.3 mmol Uatoms/cm³
 UH_3 11.1 g/cm³ 46.1 mmol Uatoms/cm³

U atom volume density expansion of 74% !!!!

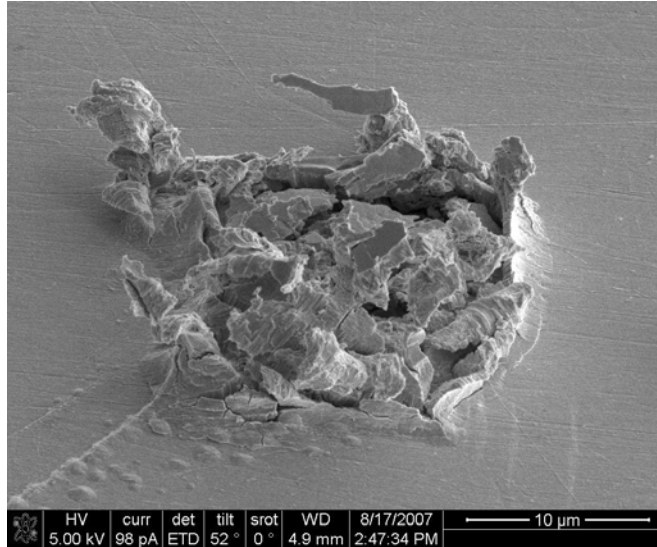
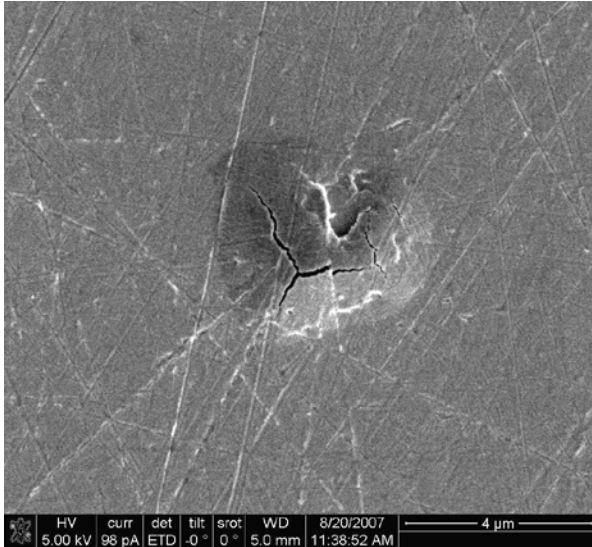
Leads to work against the surrounding metal



Uranium Hydriding Mechanism

8) Breakthrough phase of hydride –

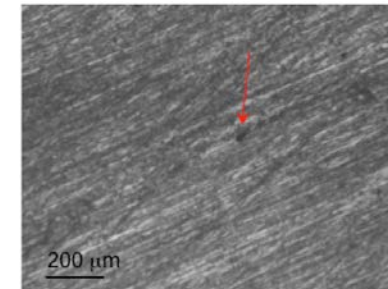
only now is the induction period complete!



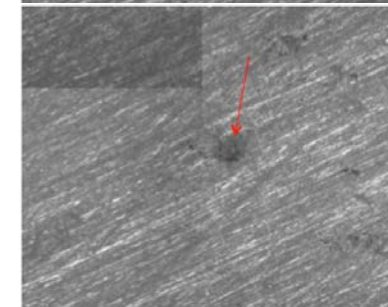
Seikhaus hydride dehydride
SEM study

Detectable first only with microscope – not by
eye on engineering surfaces

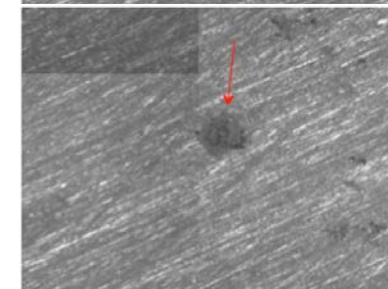
LANL parametric
room temperature
low H₂ pressure



0 days



818
days



873
days



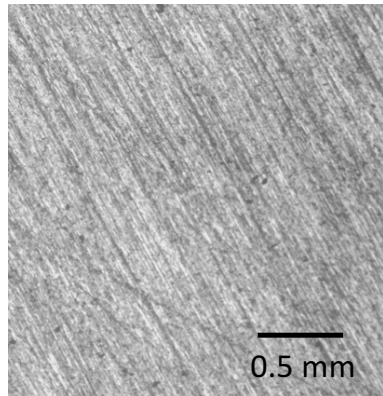
907
days

Slide 29

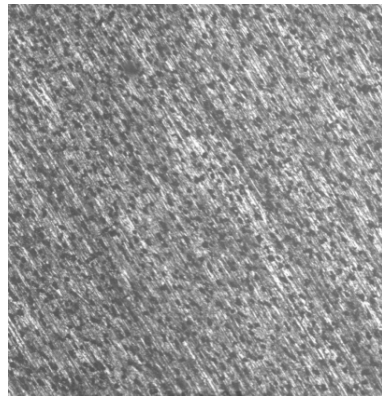
Uranium Hydriding Mechanism

8) Breakthrough phase of hydride – only now is the induction period complete!

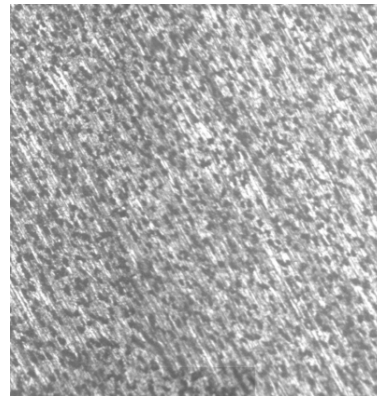
Evolution of Modes 1 and 2 Uranium Hydride Approaching Engineering-like Time Frames



0 days H₂ Exposure



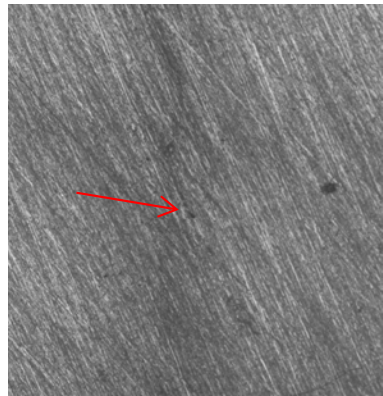
745 Days H₂ Exposure



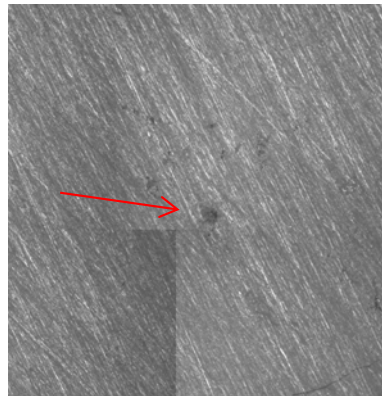
1097 days H₂ Exposure

Cell 17: 1 torr, 0.13 mm gap, inert box formed oxide

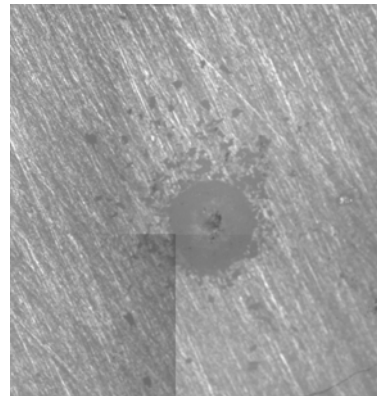
Mode 1 growth observed: Mode 1 involves the sudden appearance of very small hydrides at the surface with very slow growth over aging time. Mode 1 occurs when the hydride becomes surface exposed early on in its development, and typically many locations react with gas phase hydrogen – less localized hydrogen delivery.



0 days H₂ Exposure



819 days H₂ Exposure



908 days H₂ Exposure

Cell 19: 1 torr, contact occluded surface, air formed oxide

Mode 2 growth observed: the appearance of full subsurface hydride evolution with eventually rapid growth and blister formation leading to the hydride breakthrough phase

Over long aging times (several years), hydrides may form in the subsurface forming a virtually undetectable blister which eventually evolves to the full breakthrough stage, releasing large amounts of hydride product and grow rapidly after breakthrough.

Uranium Hydriding Mechanism

9) Direct delivery of hydrogen to site – bulk kinetic growth

10) Hydride product spall and pit formation

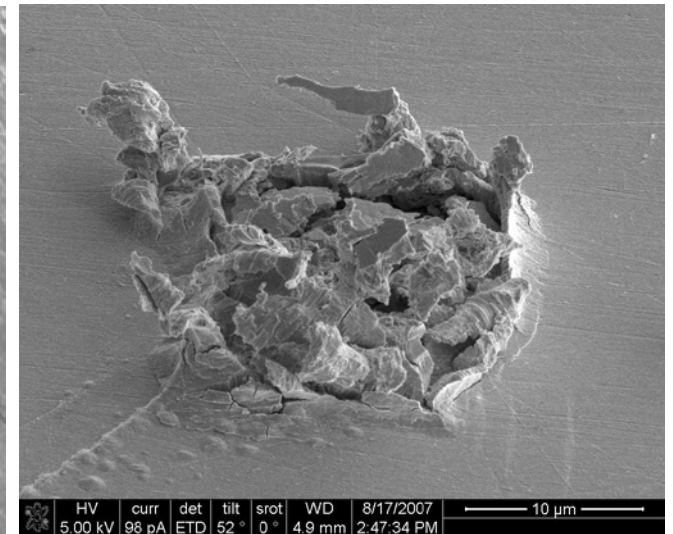
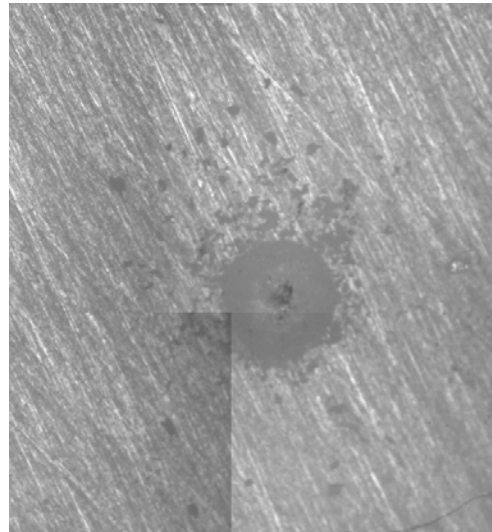
- Delivery of H₂ to reaction site now fully fast based on pressure – kinetic delivery

$$f = \frac{P}{\sqrt{2\pi MRT}}$$

- Sticking coefficient probably 1 – 0.1 unless XXX present
- UH₃ is a good solvent for H₂ – transport to the reactant U metal is rapid
- Condon Kirkpatrick kinetics now in effect

Gas pressure (torr)	Flux of molecules f (H ₂ /cm ² sec)	Monolayer time (sec)
10	1.4x10 ²²	7.0x10 ⁻⁰⁸
1	1.4x10 ²¹	7.0x10 ⁻⁰⁷
0.1	1.4x10 ²⁰	7 μsec
0.01	1.4x10 ¹⁹	7.0x10 ⁻⁰⁵
1 mtorr	1.4x10 ¹⁸	7.0x10 ⁻⁰⁴

- Pit growth in a hemispherical fashion
- Corrosion product build up, expansion, and spread
- Catastrophically destructive corrosion

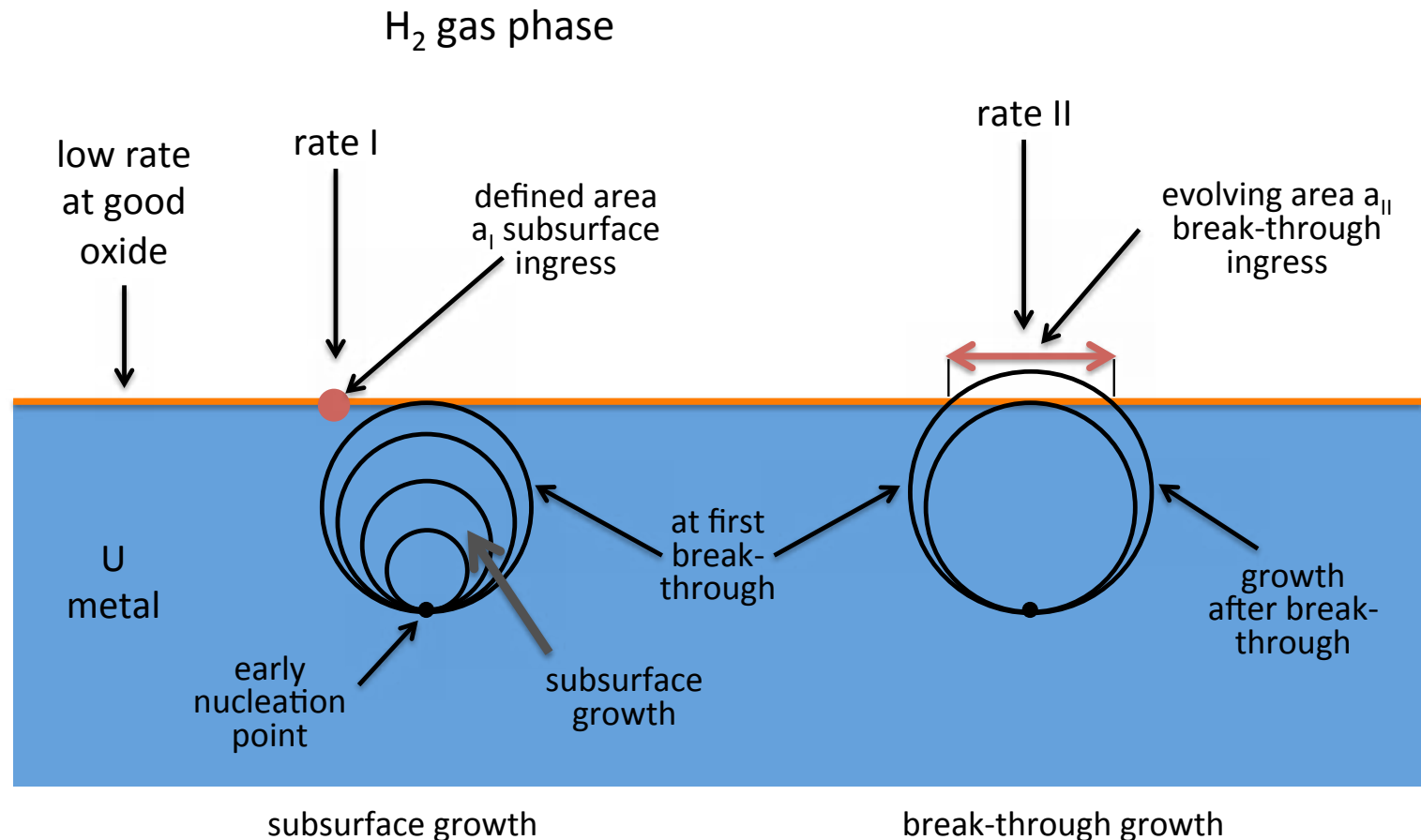


Uranium hydriding corrosion – geometric model for early stage only

molecular → mesoscopic → microscopic → mm-size

Understood as a geometric collective-parameter model that is valid only in early stages of the hydriding process

Not expected to be valid for later stage massive corrosion (>mm scale) or for cases of confined corrosion product



$$\Delta \text{moles } UH_3 = \text{rate I} \times a_I \times \Delta t$$

$$\Delta \text{volume } UH_3 (\mu m^3) = \text{moles} / 4.61 \times 10^{-14}$$

$$UH_3 \text{ diameter } d (\mu m) = (6 \times \text{volume} / \pi)^{1/3}$$

$$\Delta \text{moles } UH_3 = \text{rate II} \times a_{II}(t) \times \Delta t$$

$$\Delta \text{volume } UH_3 (\mu m^3) = \text{moles} / 4.61 \times 10^{-14}$$

$$UH_3 \text{ diameter } d (\mu m) = (6 \times \text{volume} / \pi)^{1/3}$$

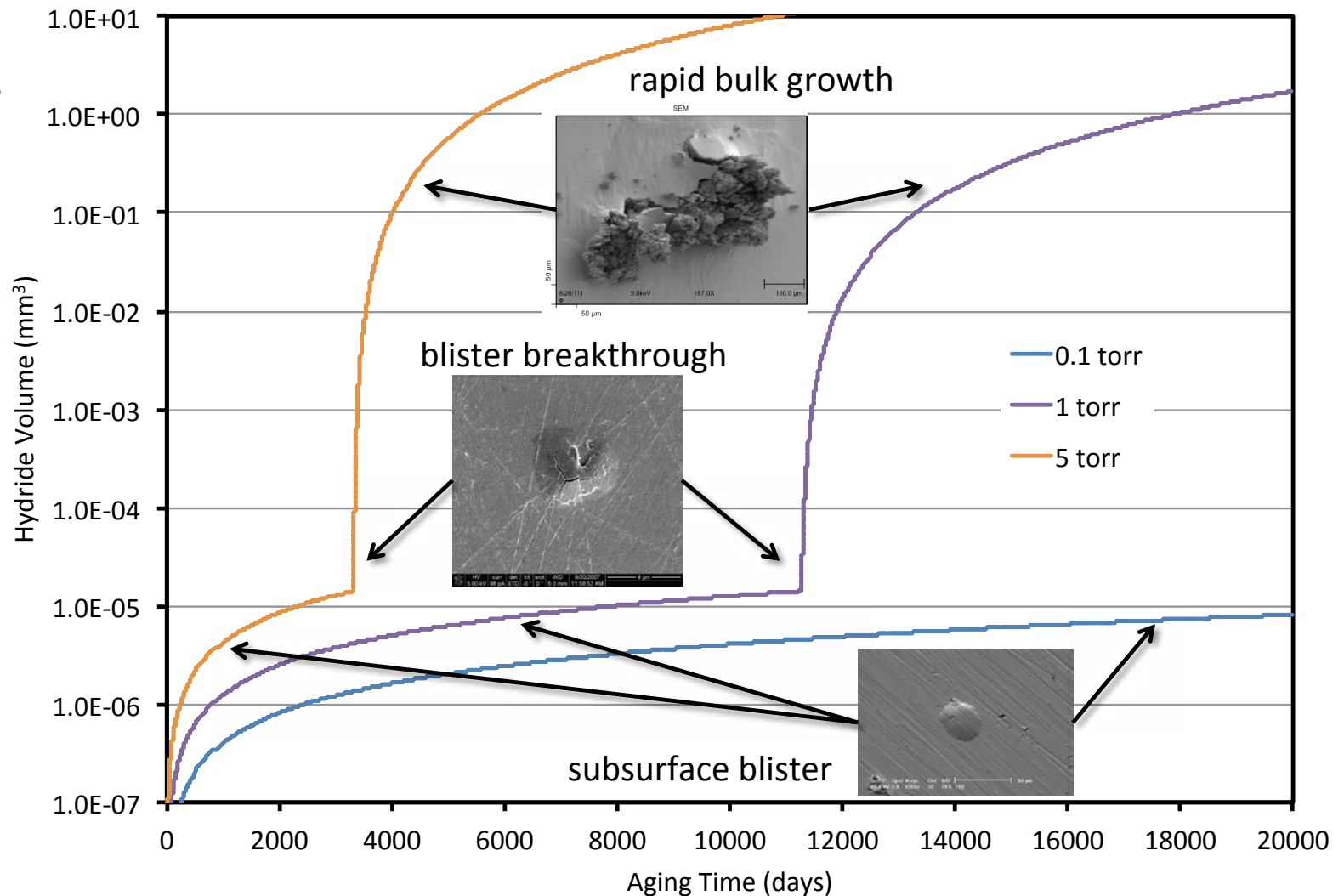
$$a_{II}(t) = \pi((d_{\text{new}}/2)^2 - (d_b/2)^2)$$

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U hydriding – some open questions

1. What are the types of defects (and which are of primary importance) in the surface thin film oxide where hydrogen is surface adsorbed and transported to the reactive subsurface metal (surface science, in-situ SEM/TEM reactions, in-situ SPM reactions)
2. For ambient conditions, what are the transport rates for hydrogen through uranium oxide(s) and uranium metal and how does the microstructure of each influence the rates (classic permeation measurements, Devanathan and Stachurski method, DFT computation)
3. What are the primary metal nucleation sites for hydride (grain boundary, metal structure defect, chemical defect, pre-existing hydride, other?) (in-situ TEM reactions, coupon post-mortem FIB studies, DFT computation)
4. What are the microscopic modes (chemical reaction details, α -UH₃ & β -UH₃, early morphological development) of subsurface hydride growth, what factors determine the mode, and below what depth is the reaction arrested (DFT computation, coupon post-mortem FIB studies)
5. How does the metal topmost surface condition (residual strain and machine work, impurity content, UO_{2±x} oxide stoichiometry, oxide condition) affect the hydriding process (coupon experiments)
6. How does the hydriding progress at the early stage of breakthrough ($\mu\text{m} \rightarrow \text{mm}$ scale) (coupon experiments, microscopy, modelling)
7. How does later stage hydriding progress for the massive corrosion ($\text{mm} \rightarrow \text{cm}$ scale), especially for confined growth of corrosion product (coupon experiments, load confined experiments, modelling)

Summary

- Corrosion behavior of uranium – needs to be well understood at the early stages: molecular, nucleation, mesoscopic, microscopic
- Using a combination of methods to understand early stage oxidation
- Using a combination of methods to understand early stage hydriding
- At surfaces non-equilibrium thermodynamics dominates behavior
- Mechanistically, for hydriding, the devil is in the details – starting at the molecular chemical level, but also involving many microstructural aspects of the material
- 10 step mechanism of hydriding can be instructive to understanding early hydriding corrosion on real world materials – covering many length scales!
- 2 primary mechanistic phases for early stage (to the micro hydriding):
 - nucleation and subsurface growth (induction phase)
 - Breakthrough phase – bulk kinetic growth (up to the microscopic and early macro scale)
- Some useful models for describing early stage hydriding behavior